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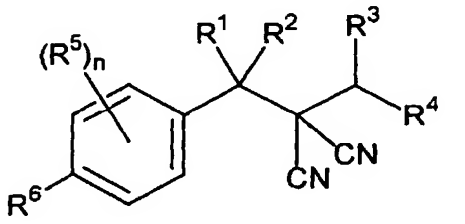
(54) Title: PESTICIDE COMPOSITION COMPRISING MALONONITRILE COMPOUNDS



(X)

(57) Abstract: The present invention relates to use of malononitrile compounds of formula (X): wherein R_1 and R_2 are the same or different and independently C^1-C^5 (halo)alkyl, C^1-C^5 (halo)alkyloxy, C^2-C^5 (halo)alkenyl, C^2-C^5 (halo)alkynyl, hydrogen, or cyano; R_3 and R_4 are the same or different and independently C^1-C^{10} alkyl, C^2-C^{10} alkenyl, C^2-C^{10} alkynyl, or hydrogen, or R_3 and R_4 are taken together to form C^2-C^6 (halo)alkylene or C^4-C^6 (halo)alkenylene; R_5 is halogen, cyano, nitro, C^1-C^4 (halo)alkyl, or the like; n is an integer of 0 to 4; R_6 is halogen, cyano, nitro, C^1-C^4 (halo)alkyl, or the like; or R_5 and R_6 are taken together to form methylenedioxy; with the provisos that when R_6 is hydrogen, then n is an integer of 1 to 4 and that when n is 2 or more, then R_5's are different from each other; as pesticides, and to pesticide compositions containing these compounds as active ingredients. The present invention makes it possible to effectively control pests such as insect pests, acarine pests, and nematode pests.

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DESCRIPTION

PESTICIDE COMPOSITION COMPRISING MALONONITRILE COMPOUNDS

Technical Field

The present invention relates to pesticide compositions comprising the malononitrile compounds as active ingredients and to use of certain malononitrile compounds as pesticides.

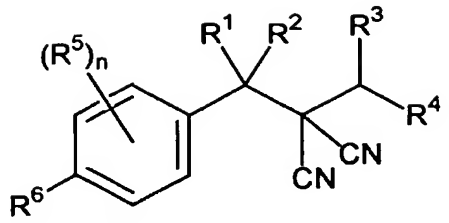
Background Art

Against pests such as insect pests, acarine pests, and nematode pests, various pesticide compositions have been used so far for their control. The conditions of pesticide compositions required have drastically been changed, including the care of their effects on the environment and the acquisition of drug resistance by pests to be controlled. Under such circumstances, there have been great demands for the development of new pesticide compositions.

Disclosure of Invention

The present inventors have extensively studied to find compounds having excellent pest controlling activity. As a result, they have found that the malononitrile compounds of formula (X) as depicted below have excellent controlling activity against pests such as insect pests, acarine pests, and nematode pests, thereby reaching the present invention.

That is, the present invention provides a pesticide composition comprising malononitrile compounds of formula (X):



(X)

(hereinafter referred to as compound(s) (X))

wherein R^1 and R^2 are the same or different and independently C_1-C_5 (halo)-alkyl, C_1-C_5 (halo)alkyloxy, C_2-C_5 (halo)alkenyl, C_2-C_5 (halo)alkynyl, hydrogen, or cyano;

R^3 and R^4 are the same or different and independently C_1-C_{10} alkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, or hydrogen, or R^3 and R^4 are taken together to form C_2-C_6 (halo)alkylene or C_4-C_6 (halo)alkenylene;

R^5 is halogen, cyano, nitro, C_1-C_4 (halo)alkyl, C_2-C_4 (halo)alkenyl, C_2-C_4 (halo)alkynyl, C_1-C_4 (halo)alkyloxy, C_1-C_4 (halo)alkylthio, C_1-C_4 (halo)-alkylsulfinyl, C_1-C_4 (halo)alkylsulfonyl, C_1-C_4 (halo)alkylcarbonyl, C_1-C_4 (halo)alkyloxycarbonyl, C_1-C_4 (halo)alkylcarbonyloxy, phenyloxy, or phenylthio, in which the phenyloxy and phenylthio groups may optionally be substituted with halogen or C_1-C_3 alkyl;

n is an integer of 0 to 4;

R^6 is hydrogen, halogen, cyano, nitro, C_1-C_4 (halo)alkyl, C_2-C_4 (halo)-alkenyl, C_2-C_4 (halo)alkynyl, C_1-C_4 (halo)alkyloxy, C_1-C_4 (halo)alkylthio, C_1-C_4 (halo)alkylsulfinyl, C_1-C_4 (halo)alkylsulfonyl, C_1-C_4 (halo)alkylcarbonyl, C_1-C_4 (halo)alkyloxycarbonyl, C_1-C_4 (halo)alkylcarbonyloxy, phenyloxy, or phenylthio, in which the phenyloxy and phenylthio groups may optionally be substituted with halogen or C_1-C_3 alkyl;

or R^5 and R^6 are taken together to form methylenedioxy;

with the provisos that when R^6 is hydrogen, then n is an integer of 1 to 4 and that when n is 2 or more, then R^5's are the same or different from each other;

as an active ingredient.

The present invention also provides use of compounds (X) as active ingredients and pest controlling methods by applying compounds (X) to pests or habitats of pests.

Mode for Carrying Out the Invention

In the definition of substituents as used herein, each group has the following meaning:

The (halo)alkyl group refers to alkyl optionally substituted with halogen for one or more than one hydrogen atoms.

The (halo)alkyloxy group refers to alkyloxy optionally substituted with halogen for one or more than one hydrogen atoms.

The (halo)alkenyl group refers to alkenyl optionally substituted with halogen for one or more than one hydrogen atoms.

The (halo)alkynyl group refers to alkynyl optionally substituted with halogen for one or more than one hydrogen atoms.

The (halo)alkylene group refers to alkylene optionally substituted with halogen for one or more than one hydrogen atoms.

The (halo)alkenylene group refers to alkenylene optionally substituted with halogen for one or more than one hydrogen atoms.

The (halo)alkylthio group refers to alkylthio optionally substituted with halogen for one or more than one hydrogen atoms.

The (halo)alkylsulfinyl group refers to alkylsulfinyl optionally substituted with halogen for one or more than one hydrogen atoms.

The (halo)alkylsulfonyl group refers to alkylsulfonyl optionally substituted with halogen for one or more than one hydrogen atoms.

The (halo)alkylcarbonyl group refers to alkylcarbonyl optionally substituted with halogen for one or more than one hydrogen atoms.

The (halo)alkyloxycarbonyl group refers to alkyloxycarbonyl option-

ally substituted with halogen for one or more than one hydrogen atoms.

The (halo)alkylcarbonyloxy group refers to alkylcarbonyloxy optionally substituted with halogen for one or more than one hydrogen atoms.

The term "C_1-C_{10}" or the like refers to the number of carbon atoms constituting the alkyl, alkenyl, or alkynyl group in each substituent. For example, C_1-C_4 (halo)alkylcarbonyl means alkylcarbonyl optionally substituted with halogen for one or more hydrogen atoms wherein the alkyl part is constituted by C_1-C_4 carbon atoms.

In compounds (X), each group includes specific ones as listed below:

The C_1-C_5 (halo)alkyl group represented by R^1 or R^2 may include methyl, ethyl, propyl, 1-methylethyl, 1,1-dimethylethyl, 2,2-dimethylpropyl, chloromethyl, fluoromethyl, difluoromethyl, trifluoromethyl, 2,2,2-trifluoroethyl, and 1,1,2,2-tetrafluoroethyl.

The C_1-C_5 (halo)alkyloxy group represented by R^1 or R^2 may include methoxy, ethoxy, 1-methylethoxy, trifluoromethoxy, difluoromethoxy, 2,2,2-trifluoroethoxy, and 1,1,2,2-tetrafluoroethoxy.

The C_2-C_5 (halo)alkenyl group represented by R^1 or R^2 may include vinyl, 1-propenyl, 2-propenyl, 2,2-difluorovinyl, and 1,2,2-trifluorovinyl.

The C_2-C_5 (halo)alkynyl group represented by R^1 or R^2 may include ethynyl, 1-propynyl, 2-propynyl and 3,3,3-trifluoro-1-propynyl.

The C_1-C_{10} alkyl group represented by R^3 or R^4 may include methyl, ethyl, 1-methylethyl, propyl, 2-methylpropyl, 2,2-dimethylpropyl, butyl, 3-methylbutyl, and 3,3-dimethylbutyl.

The C_2-C_{10} alkenyl group represented by R^3 or R^4 may include vinyl, allyl, 1-propenyl, 3-butenyl, 2-methyl-1-propenyl, 3-methyl-2-butenyl, 3-pentenyl, 4-pentenyl, 3-methyl-3-butenyl, and 4-methyl-3-pentenyl.

The C_2-C_{10} alkynyl group represented by R^3 or R^4 may include ethynyl, 1-propynyl, 2-propynyl, 1-butynyl, 3-methyl-1-butynyl, and 3,3-di-

methyl-1-butynyl.

The C_2-C_6 (halo)alkylene group represented by R^3 and R^4 taken together may include ethylene, propylene, trimethylene, tetramethylene, and 3,3-dimethyltrimethylene.

The C_4-C_6 (halo)alkenylene group represented by R^3 and R^4 taken together may include 2-butenylene and 2-pentenylene.

The halogen atom represented by R^5 or R^6 may include fluorine, chlorine, bromine, and iodine.

The C_1-C_4 (halo)alkyl group represented by R^5 or R^6 may include methyl, ethyl, propyl, 1-methylethyl, 1,1-dimethylethyl, trifluoromethyl, pentafluoroethyl, 3,3,3-trifluoroethyl, and 1,1,2,2-tetrafluoroethyl.

The C_2-C_4 (halo)alkenyl group represented by R^5 or R^6 may include vinyl, 1-propenyl, 2-propenyl and 2,2-difluorovinyl.

The C_2-C_4 (halo)alkynyl group represented by R^5 or R^6 may include ethynyl, 1-propynyl, 2-propynyl and 3,3,3-trifluoro-1-propynyl.

The C_1-C_4 (halo)alkyloxy group represented by R^5 or R^6 may include methoxy, ethoxy, propoxy, trifluoromethoxy, bromodifluoromethoxy, difluoromethoxy, chlorodifluoromethoxy, pentafluoroethoxy, 2,2,2-trifluoroethoxy, and 1,1,2,2-tetrafluoroethoxy.

The C_1-C_4 (halo)alkylthio group represented by R^5 or R^6 may include methylthio, trifluoromethylthio, 2,2,2-trifluoroethylthio, and 1,1,2,2-tetrafluoroethylthio.

The C_1-C_4 (halo)alkylsulfinyl group represented by R^5 or R^6 may include methylsulfinyl and trifluoromethylsulfinyl.

The C_1-C_4 (halo)alkylsulfonyl group represented by R^5 or R^6 may include methylsulfonyl and trifluoromethylsulfonyl.

The C_1-C_4 (halo)alkylcarbonyl group represented by R^5 or R^6 may include acetyl, propionyl, and trifluoroacetyl.

The C_1-C_4 (halo)alkyloxycarbonyl group represented by R^5 or R^6 may include methoxycarbonyl and 2,2,2-trifluoroethoxycarbonyl.

The C_1-C_4 (halo)alkylcarbonyloxy group represented by R^5 or R^6 may include acetyloxy, propionyloxy, and trifluoroacetyloxy.

The phenyloxy optionally substituted with halogen or C_1-C_3 alkyl, which is represented by R^5 or R^6, may include phenoxy, p-methylphenoxy, m-methylphenoxy, and p-chlorophenoxy.

The phenylthio group optionally substituted with halogen or C_1-C_3 alkyl, which is represented by R^5 or R^6, may include phenylthio, p-methylphenylthio, m-methylphenylthio, and p-chlorophenylthio.

The embodiments of compounds (X) may include the following compounds:

The malononitrile compounds of formula (X) wherein R^1 is hydrogen, and R^2 is C_1-C_5 (halo)alkyl, C_2-C_5 (halo)alkenyl, or hydrogen;

The malononitrile compounds of formula (X) wherein R^1 and R^2 are both hydrogen;

The malononitrile compounds of formula (X) wherein R^3 is C_1-C_{10} alkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, or hydrogen; R^4 is C_1-C_{10} alkyl, C_2-C_{10} alkenyl, or C_2-C_{10} alkynyl;

The malononitrile compounds of formula (X) wherein R^3 is hydrogen and R^4 is C_1-C_{10} alkyl, C_2-C_{10} alkenyl, or C_2-C_{10} alkynyl;

The malononitrile compounds of formula (X) wherein R^3 is hydrogen and R^4 is C_1-C_{10} alkyl or C_2-C_{10} alkenyl;

The malononitrile compounds of formula (X) wherein R^3 is hydrogen and R^4 is C_1-C_{10} alkyl;

The malononitrile compounds of formula (X) wherein R^5 is halogen, n is an integer of 0 to 2;

The malononitrile compounds of formula (X) wherein R^6 is halogen,

cyano, nitro, C_1-C_4 haloalkyl, C_1-C_4 haloalkyloxy, or C_1-C_4 haloalkylthio;

The malononitrile compounds of formula (X) wherein R^5 is halogen, n is an integer of 0 to 2, and R^6 is halogen, cyano, nitro, C_1-C_4 (halo)alkyl, C_1-C_4 (halo)alkyloxy, or C_1-C_4 (halo) alkylthio;

The malononitrile compounds of formula (X) wherein R^3 is hydrogen; R^4 is C_1-C_{10} alkyl, C_2-C_{10} alkenyl, or C_2-C_{10} alkynyl, R^5 is halogen, n is an integer of 0 to 2, and R^6 is halogen, cyano, nitro, C_1-C_4 (halo)alkyl, C_1-C_4 (halo)alkyloxy, or C_1-C_4 (halo) alkylthio;

The malononitrile compounds of formula (X) wherein R^1 is hydrogen, R^2 is C_1-C_5 (halo)alkyl, C_2-C_5 (halo)alkenyl, or hydrogen, R^3 is hydrogen; R^4 is C_1-C_{10} alkyl, C_2-C_{10} alkenyl, or C_2-C_{10} alkynyl, R^5 is halogen, n is an integer of 0 to 2, and R^6 is halogen, cyano, nitro, C_1-C_4 (halo)alkyl, C_1-C_4 (halo)alkyloxy, or C_1-C_4 (halo) alkylthio;

The malononitrile compounds of formula (X) wherein R^4 is vinyl and R^6 is trifluoromethyl;

The malononitrile compounds of formula (X) wherein R^4 is vinyl and R^6 is difluoromethoxy;

The malononitrile compounds of formula (X) wherein R^4 is vinyl and R^6 is trifluoromethoxy;

The malononitrile compounds of formula (X) wherein R^4 is vinyl and R^6 is trifluoromethylthio;

The malononitrile compounds of formula (X) wherein R^4 is vinyl and R^6 is 1,1,2,2-tetrafluoroethoxy;

The malononitrile compounds of formula (X) wherein R^4 is vinyl and R^6 is chlorine;

The malononitrile compounds of formula (X) wherein R^4 is vinyl and R^6 is bromine;

The malononitrile compounds of formula (X) wherein R^4 is vinyl and

R^6 is fluorine;

The malononitrile compounds of formula (X) wherein R^4 is vinyl and R^6 is cyano;

The malononitrile compounds of formula (X) wherein R^4 is vinyl and R^6 is nitro;

The malononitrile compounds of formula (X) wherein R^4 is allyl and R^6 is trifluoromethyl;

The malononitrile compounds of formula (X) wherein R^4 is allyl and R^6 is difluoromethoxy;

The malononitrile compounds of formula (X) wherein R^4 is allyl and R^6 is trifluoromethoxy;

The malononitrile compounds of formula (X) wherein R^4 is allyl and R^6 is trifluoromethylthio;

The malononitrile compounds of formula (X) wherein R^4 is allyl and R^6 is 1,1,2,2-tetrafluoroethoxy;

The malononitrile compounds of formula (X) wherein R^4 is allyl and R^6 is chlorine;

The malononitrile compounds of formula (X) wherein R^4 is allyl and R^6 is bromine;

The malononitrile compounds of formula (X) wherein R^4 is allyl and R^6 is fluorine;

The malononitrile compounds of formula (X) wherein R^4 is allyl and R^6 is cyano;

The malononitrile compounds of formula (X) wherein R^4 is allyl and R^6 is nitro;

The malononitrile compounds of formula (X) wherein R^4 is ethyl and R^6 is trifluoromethyl;

The malononitrile compounds of formula (X) wherein R^4 is ethyl and

R^6 is trifluoromethoxy;

The malononitrile compounds of formula (X) wherein R^4 is ethyl and R^6 is trifluoromethylthio;

The malononitrile compounds of formula (X) wherein R^4 is ethyl and R^6 is chlorine;

The malononitrile compounds of formula (X) wherein R^4 is ethyl and R^6 is cyano;

The malononitrile compounds of formula (X) wherein R^4 is 3-butenyl and R^6 is trifluoromethyl;

The malononitrile compounds of formula (X) wherein R^4 is 3-butenyl and R^6 is trifluoromethoxy;

The malononitrile compounds of formula (X) wherein R^4 is 3-butenyl and R^6 is trifluoromethylthio;

The malononitrile compounds of formula (X) wherein R^4 is 3-butenyl and R^6 is chlorine;

The malononitrile compounds of formula (X) wherein R^4 is 3-butenyl and R^6 is cyano;

The malononitrile compounds of formula (X) wherein R^4 is 2-methyl-1-propenyl and R^6 is trifluoromethyl;

The malononitrile compounds of formula (X) wherein R^4 is 2-methyl-1-propenyl and R^6 is trifluoromethoxy;

The malononitrile compounds of formula (X) wherein R^4 is 2-methyl-1-propenyl and R^6 is trifluoromethylthio;

The malononitrile compounds of formula (X) wherein R^4 is 2-methyl-1-propenyl and R^6 is chlorine;

The malononitrile compounds of formula (X) wherein R^4 is 2-methyl-1-propenyl and R^6 is cyano;

The malononitrile compounds of formula (X) wherein R^4 is 1-propenyl

and R^6 is trifluoromethyl;

The malononitrile compounds of formula (X) wherein R^4 is 1-propenyl and R^6 is trifluoromethoxy;

The malononitrile compounds of formula (X) wherein R^4 is 1-propenyl and R^6 is trifluoromethylthio;

The malononitrile compounds of formula (X) wherein R^4 is 1-propenyl and R^6 is chlorine;

The malononitrile compounds of formula (X) wherein R^4 is 1-propenyl and R^6 is cyano;

The malononitrile compounds of formula (X) wherein R^4 is 2-methylpropyl and R^6 is trifluoromethyl;

The malononitrile compounds of formula (X) wherein R^4 is 2-methylpropyl and R^6 is difluoromethoxy;

The malononitrile compounds of formula (X) wherein R^4 is 2-methylpropyl and R^6 is trifluoromethoxy;

The malononitrile compounds of formula (X) wherein R^4 is 2-methylpropyl and R^6 is trifluoromethylthio;

The malononitrile compounds of formula (X) wherein R^4 is 2-methylpropyl and R^6 is 1,1,2,2-tetrafluoroethoxy;

The malononitrile compounds of formula (X) wherein R^4 is 2-methylpropyl and R^6 is chlorine;

The malononitrile compounds of formula (X) wherein R^4 is 2-methylpropyl and R^6 is bromine;

The malononitrile compounds of formula (X) wherein R^4 is 2-methylpropyl and R^6 is fluorine;

The malononitrile compounds of formula (X) wherein R^4 is 2-methylpropyl and R^6 is cyano;

The malononitrile compounds of formula (X) wherein R^4 is 2-methyl-

propyl and R^6 is nitro;

The malononitrile compounds of formula (X) wherein R^4 is 2,2-dimethylpropyl and R^6 is trifluoromethyl;

The malononitrile compounds of formula (X) wherein R^4 is 2,2-dimethylpropyl and R^6 is difluoromethoxy;

The malononitrile compounds of formula (X) wherein R^4 is 2,2-dimethylpropyl and R^6 is trifluoromethoxy;

The malononitrile compounds of formula (X) wherein R^4 is 2,2-dimethylpropyl and R^6 is trifluoromethylthio;

The malononitrile compounds of formula (X) wherein R^4 is 2,2-dimethylpropyl and R^6 is 1,1,2,2-tetrafluoroethoxy;

The malononitrile compounds of formula (X) wherein R^4 is 2,2-dimethylpropyl and R^6 is chlorine;

The malononitrile compounds of formula (X) wherein R^4 is 2,2-dimethylpropyl and R^6 is bromine;

The malononitrile compounds of formula (X) wherein R^4 is 2,2-dimethylpropyl and R^6 is fluorine;

The malononitrile compounds of formula (X) wherein R^4 is 2,2-dimethylpropyl and R^6 is cyano;

The malononitrile compounds of formula (X) wherein R^4 is 2,2-dimethylpropyl and R^6 is nitro;

The malononitrile compounds of formula (X) wherein R^4 is 1-methylethyl and R^6 is trifluoromethyl;

The malononitrile compounds of formula (X) wherein R^4 is 1-methylethyl and R^6 is difluoromethoxy;

The malononitrile compounds of formula (X) wherein R^4 is 1-methylethyl and R^6 is trifluoromethoxy;

The malononitrile compounds of formula (X) wherein R^4 is 1-methyl-

ethyl and R^6 is trifluoromethylthio;

The malononitrile compounds of formula (X) wherein R^4 is 1-methyl-ethyl and R^6 is 1,1,2,2-tetrafluoroethoxy;

The malononitrile compounds of formula (X) wherein R^4 is 1-methyl-ethyl and R^6 is chlorine;

The malononitrile compounds of formula (X) wherein R^4 is 1-methyl-ethyl and R^6 is bromine;

The malononitrile compounds of formula (X) wherein R^4 is 1-methyl-ethyl and R^6 is fluorine;

The malononitrile compounds of formula (X) wherein R^4 is 1-methyl-ethyl and R^6 is cyano;

The malononitrile compounds of formula (X) wherein R^4 is 1-methyl-ethyl and R^6 is nitro.

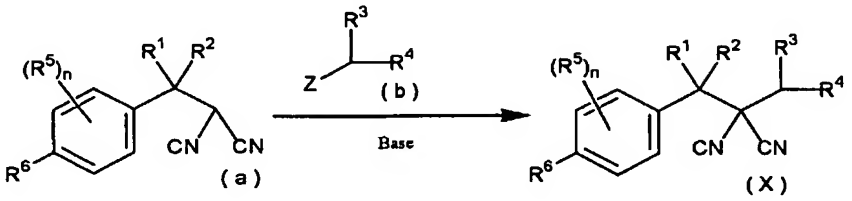
The preferred compounds among compound (X) are the compounds wherein R^6 is halogen, cyano, nitro, C_1-C_4 haloalkyl, C_1-C_4 haloalkyloxy or C_1-C_4 haloalkylthio; the compounds wherein R^3 and R^4 are the same or different and independently C_1-C_5 alkyl, C_2-C_5 alkenyl, C_2-C_5 alkynyl, or hydrogen, or R^3 and R^4 are taken together to form C_2-C_6 (halo)alkylene; or the compounds wherein n is 1 to 3 and at least one of R^5 is halogen, cyano, nitro, C_1-C_4 haloalkyl, C_1-C_4 haloalkyloxy or C_1-C_4 (halo)alkylthio. More preferred compounds are the compounds wherein R^6 is halogen, cyano, nitro, C_1-C_4 fluoroalkyl, C_1-C_4 fluoroalkyloxy or C_1-C_4 fluoroalkylthio; or the compounds wherein n is 1 to 3 and at least one of R^5 is halogen, cyano, nitro, C_1-C_4 fluoroalkyl, C_1-C_4 fluoroalkyloxy or C_1-C_4 fluoroalkylthio.

The following will describe the production processes for compounds (X).

The compounds (X) can be produced by, for example, the following (Production Process 1) to (Production Process 5).

(Production Process 1)

This is a process by reacting compound (a) with compound (b) in the presence of a base.



wherein R^1, R^2, R^3, R^4, R^5, R^6, and n are as defined above, and Z is halogen, methanesulfonyl, trifluoromethanesulfonyl, or toluenesulfonyl.

The reaction is usually carried out in a solvent. The solvent which can be used in the reaction may include acid amides such as dimethylformamide; ethers such as diethyl ether and tetrahydrofuran; organic sulfur compounds such as dimethylsulfoxide and sulfolane; halogenated hydrocarbons such as 1,2-dichloroethane and chlorobenzene; aromatic hydrocarbons such as toluene and xylene; water; and mixtures thereof.

The base which can be used in the reaction may include inorganic bases such as sodium hydride, sodium hydroxide, potassium hydroxide, and potassium carbonate; alkali metal alkoxides such as sodium methoxide, sodium ethoxide, and potassium tert-butoxide; alkali metal amides such as lithium diisopropylamide; and organic bases such as 4-dimethylaminopyridine, 1,4-diazabicyclo[2.2.2]octane, and 1,8-diazabicylco[5.4.0]-7-undecene. The amount of base used in the reaction is usually in a ratio of 1 to 10 moles relative to 1 mole of compound (a).

The reaction temperature is usually in the range of –20°C to 100°C.

The reaction time is usually in the range of 1 to 24 hours.

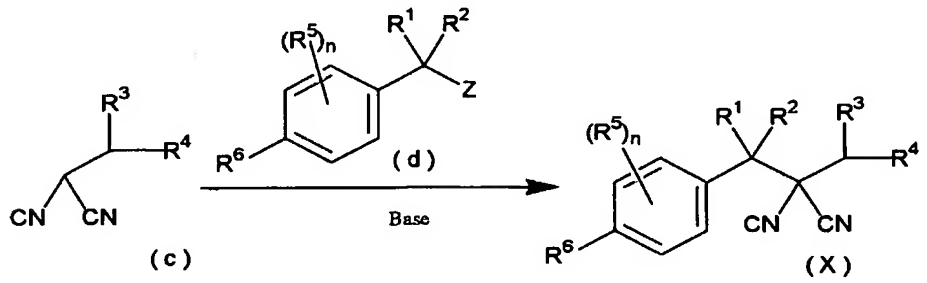
The amount of compound (b) used in the reaction is usually in a ratio of 1 to 10 moles relative to 1 mole of compound (a).

After the reaction, the reaction mixture is poured into water, followed

by ordinary post-treatment procedures including extraction with an organic solvent and concentration, thereby isolating the desired compounds, which may be purified by a technique such as chromatography or recrystallization.

(Production Process 2)

This is a process by reacting compound (c) with compound (d) in the presence of a base.



wherein R^1, R^2, R^3, R^4, R^5, R^6, n, and Z are as defined above.

The reaction is usually carried out in a solvent. The solvent which can be used in the reaction may include acid amides such as dimethylformamide; ethers such as diethyl ether and tetrahydrofuran; organic sulfur compounds such as dimethylsulfoxide and sulfolane; halogenated hydrocarbons such as 1,2-dichloroethane and chlorobenzene; aromatic hydrocarbons such as toluene and xylene; water; and mixtures thereof.

The base which can be used in the reaction may include inorganic bases such as sodium hydride, sodium hydroxide, potassium hydroxide, and potassium carbonate; alkali metal alkoxides such as sodium methoxide, sodium ethoxide, and potassium tert-butoxide; alkali metal amides such as lithium diisopropylamide; and organic bases such as 4-dimethylaminopyridine, 1,4-diazabicyclo[2.2.2]octane, and 1,8-diazabicylco[5.4.0]-7-undecene. The amount of base used in the reaction is usually in a ratio of 1 to 10 moles relative to 1 mole of compound (a).

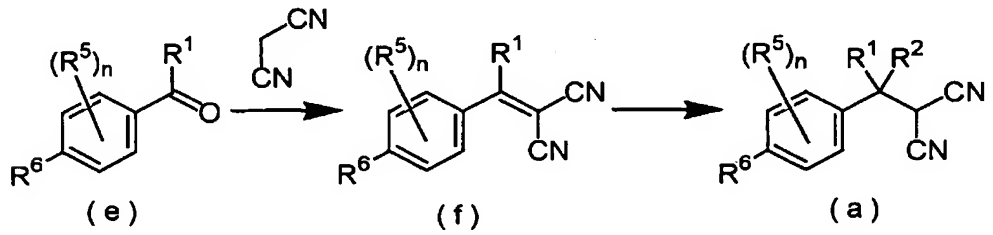
The reaction temperature is usually in the range of –20°C to 100°C.

The reaction time is usually in the range of 1 to 24 hours.

The amount of compound (b) used in the reaction is usually in a ratio of 1 to 10 moles relative to 1 mole of compound (a).

After the reaction, the reaction mixture is poured into water, followed by ordinary post-treatment procedures including extraction with an organic solvent and concentration, thereby isolating the desired compounds, which may be purified by a technique such as chromatography or recrystallization.

The compound (a) can be produced through a route, for example, as shown in the following scheme.



wherein R^1, R^2, R^5, R^6, and n are as defined above.

(Step 1)

The compound (f) can be produced by reacting compound (e) with malononitrile.

The reaction is usually carried out in a solvent and in the presence of a base. The solvent which can be used in the reaction may include acid amides such as N,N-dimethylformamide; ethers such as diethyl ether and tetrahydrofuran; halogenated hydrocarbons such as chloroform, 1,2-dichloroethane, and chlorobenzene; aromatic hydrocarbons such as toluene and xylene; alcohols such as methanol, ethanol, and isopropanol; and mixtures thereof.

The base which can be used in the reaction may include tetrabutylammonium hydroxide. The amount of base used in the reaction is usually in a ratio of 0.01 to 0.5 mole relative to 1 mole of compound (e).

The amount of malononitrile used in the reaction is usually in a ratio of 1 to 10 moles relative to 1 mole of compound (e).

The reaction temperature is usually in the range of –20°C to 200°C.

The reaction time is usually in the range of 1 to 24 hours.

The reaction may be carried out, while removing, if necessary, water which is generated by the reaction, from the reaction system.

After the reaction, the reaction mixture is poured into water, followed by ordinary post-treatment procedures including extraction with an organic solvent and concentration, thereby isolating the desired compounds, which may be purified by a technique such as chromatography or recrystallization.

(Step 2)

(1) The case where R^2 is a substituent other than hydrogen and cyano:

The compound (a) can be produced by reacting compound (f) with an organometallic compound.

The reaction is usually carried out in a solvent and, if necessary, in the presence of a copper salt.

The solvent which can be used in the reaction may include ethers such as diethyl ether and tetrahydrofuran; aromatic hydrocarbons such as toluene and xylene; and mixtures thereof.

The organometallic compound which can be used in the reaction may include organic magnesium compounds such as methyl magnesium iodide, ethyl magnesium bromide, isopropyl magnesium bromide, vinyl magnesium bromide, ethynyl magnesium bromide, and dimethyl magnesium; organic lithium compounds such as methyl lithium; organic zinc compounds such as diethyl zinc; and organic copper compounds such as trifluoromethyl copper. The amount of organometallic compound used in the reaction is usually in a ratio of 1 to 10 moles relative to 1 mole of compound (f).

The copper salt which can be used in the reaction may include copper (I) iodide and copper (I) bromide. The amount of copper salt used in the reaction is usually not greater than 1 mole relative to 1 mole of compound (f).

The reaction temperature is usually in the range of –20°C to 100°C.

The reaction time is usually in the range of 1 to 24 hours.

After the reaction, the reaction mixture is poured into water, followed by ordinary post-treatment procedures including extraction with an organic solvent and concentration, thereby isolating the desired compounds, which may be purified by a technique such as chromatography or recrystallization.

(2) The case where R^2 is hydrogen:

The compound (a) can be produced by subjecting compound (f) to reduction.

The reduction is usually carried out in a solvent.

The solvent which can be used in the reaction may include ethers such as diethyl ether and tetrahydrofuran; aromatic hydrocarbons such as toluene and xylene; alcohols such as methanol, ethanol, and propanol; water; and mixtures thereof.

The reducing agent which can be used in the reaction may include sodium borohydride. The amount of reducing agent used in the reaction is usually in a ratio of 0.25 to 2 moles relative to 1 mole of compound (f).

The reaction time is usually in the range of a moment to 24 hours.

The reaction temperature is usually in the range of 0°C to 50°C.

After the reaction, the reaction mixture is poured into water, followed by ordinary post-treatment procedures including extraction with an organic solvent and concentration, thereby isolating the desired compounds, which may be purified by a technique such as chromatography or recrystallization.

(3) The case where R^2 is cyano:

The compound (a) can be produced by reacting compound (f) with a

cyanide.

The solvent which can be used in the reaction may include ethers such as diethyl ether and tetrahydrofuran; aromatic hydrocarbons such as toluene and xylene; and mixtures thereof.

The cyanide which can be used in the reaction may include tetrabutylammonium cyanide. The amount of cyanide used in the reaction is usually in a ratio of 1 to 10 moles relative to 1 mole of compound (f).

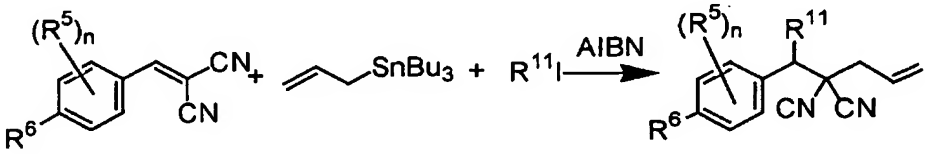
The reaction temperature is usually in the range of –20°C to 100°C.

The reaction time is usually in the range of 1 to 24 hours.

After the reaction, the reaction mixture is poured into water, followed by ordinary post-treatment procedures including extraction with an organic solvent and concentration, thereby isolating the desired compounds, which may be purified by a technique such as chromatography or recrystallization.

(Production Process 3)

The compounds wherein R^1 is C_1-C_6 (halo)alkyl, R^2 and R^3 are both hydrogen, and R^4 is CH_2=CH can also be produced by the process as shown in the following scheme.



(h) (i) (j) (k)

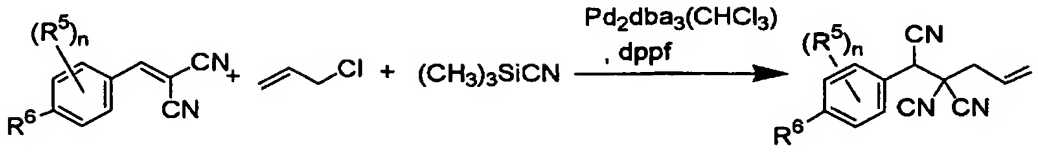
wherein R^5, R^6, and n are as defined above, R^{11} is C_1-C_6 (halo)alkyl, Bu is butyl, and AIBN is azobisisobutyronitrile.

The reaction can be carried out according to the process as described in J. Am. Chem. Soc., 110, 1289 (1988).

(Production Process 4)

The compounds wherein R^1 is cyano, R^2 and R^3 are both hydrogen, R^4

is CH_2=CH can also be produced by the process as shown in the following scheme.



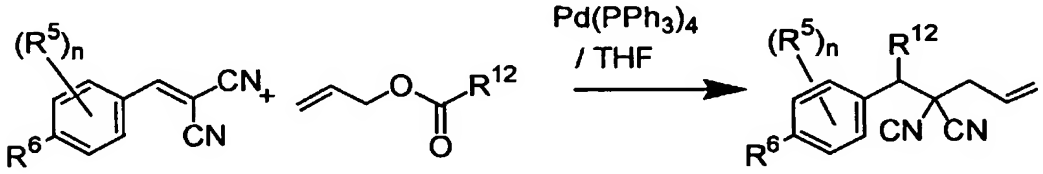
(h) (l) (m) (n)

wherein R^5, R^6, and n are as defined above, dba is dibenzylideneacetone, and dppf is 1,1'-bis(diphenylphosphino)ferrocene.

The reaction can be carried out according to the conditions as described in Tetrahedron Lett., 41, 2911 (2000).

(Production Process 5)

The compounds wherein R^1 is C_1-C_5 (halo)alkyloxy, R^2 and R^3 are both hydrogen, and R^4 is CH_2=CH can also be produced by the process as shown in the following scheme.



(h) (o) (p)

wherein R^5, R^6, and n are as defined above, R^{12} is C_1-C_5 (halo)alkyloxy, Ph is phenyl, and THF is tetrahydrofuran.

The reaction can be carried out according to the conditions as described in J. Am. Chem. Soc., 120, 6838 (1998).

The pests against which compounds (X) exhibit controlling activity may include insect pests, acarine pests, and nematode pests, specific examples which are as follows:

Hemiptera:

Delphacidae such as *Laodelphax striatellus*, *Nilaparvata lugens*, and

Sogatella furcifera;

Deltocephalidae such as *Nephotettix cincticeps* and *Nephotettix virescens*;

Aphididae such as *Aphis gossypii* and *Myzus persicae*;

Pentatomidae such as *Nezara antennata*, *Riptortus clavetus Eysarcoris lewisi*, *Eysarcoris parvus*, *Plautia stali* and *Halyomorpha misia*;

Aleyrodidae such as *Trialeurodes vaporariorum* and *Bemisia argentifolii*;

Coccidae such as *Aonidiella aurantii*, *Comstockaspis perniciosa*, *Unaspis citri*, *Ceroplastes rubens*, and *Icerya purchasi*;

Tingidae;

Psyllidae;

Lepidoptera:

Pyralidae such as *Chilo suppressalis*, *Cnaphalocrocis medinalis*, *Notarcha derogata*, and *Plodia interpunctella*;

Noctuidae such as *Spodoptera litura*, *Pseudaletia separata*, Thoricoplusia spp., Heliothis spp., and Helicoverpa spp.;

Pieridae such as *Pieris rapae*;

Tortricidae such as Adoxophyes spp., *Grapholita molesta*, and *Cydia pomonella*;

Carposinidae such as *Carposina niponensis*;

Lyonetiidae such as Lyonetia spp.;

Lymantriidae such as Lyamantria spp. and Euproctis spp.;

Yponomentidae such as *Plutella xylostella*;

Gelechiidae such as *Pectinophora gossypiella*;

Arctiidae such as *Hyphantria cunea*;

Tineidae such as *Tinea translucens* and *Tineola bisselliella*;

Diptera:

Calicidae such as *Culex pipiens pallens*, *Culex tritaeniorhynchus*, and *Culex quinquefasciatus*;

Aedes spp. such as *Aedes aegypti* and *Aedes albopictus*;

Anopheles spp. such as *Anopheles sinensis*;

Chironomidae;

Muscidae such as *Musca domestica* and *Muscina stabulans*;

Calliphoridae;

Sarcophagidae;

Fanniidae;

Anthomyiidae such as *Delia platura* and *Delia antiqua*;

Tephritidae;

Drosophilidae;

Psychodidae;

Simuliidae;

Tabanidae;

Stomoxyidae;

Agromyzidae;

Coleoptera:

Diabrotica spp. such as *Diabrotica virgifera* and *Diabrotica undecimpunctata howardi*;

Scarabaeidae such as *Anomala cuprea* and *Anomala rufocuprea*;

Curculionidae such as *Sitophilus zeamais*, *Lissorhoptrus oryzophilus*, and *Callosobruchuys chienensis*;

Tenebrionidae such as *Tenebrio molitor* and *Tribolium castaneum*;

Chrysomelidae such as *Oulema oryzae*, *Aulacophora femoralis*, *Phyllotreta striolata*, and *Leptinotarsa decemlineata*;

Anobiidae;

Epilachna spp. such as *Epilachna vigintioctopunctata*;

Lyctidae;

Bostrychidae;

Cerambycidae;

Paederus fuscipes;

Dictyoptera:

Blattella germanica, *Periplaneta fuliginosa*, *Periplaneta americana*, *Periplaneta brunnea*, and *Blatta orientalis*;

Thysanoptera:

Thrips palmi, *Thrips tabaci*, *Frankliniella occidentalis*, *Frankliniella intonsa*;

Hymenoptera:

Formicidae;

Vespidae;

Bethylidae;

Tenthredinidae such as *Athalia japonica*;

Orthoptera:

Gryllotalpidae;

Acrididae;

Siphonaptera:

Ctenocephalides felis, *Ctenocephalides canis*, *Pulex irritans*, *Xenopsylla cheopis*;

Anoplura:

Pediculus humanus corporis, *Phthirus pubis*, *Haematopinus eurysternus*, and *Dalmalinia ovis*;

Isoptera:

Reticulitermes speratus and *Coptotermes formosanus*;

Acarina:

Tetranychidae such as *Tetranychus urticae*, *Tetranychus kanzawai*,

Panonychus citri, *Panonychus ulmi*, and Oligonychus spp.;

Eriophyidae such as *Aculops pelekassi* and *Aculus schlechtendali*;

Tarsonemidae such as *Polyphagotarsonemus latus*;

Tenuipalpidae;

Tuckerellidae;

Ixodidae such as *Haemaphysalis longicornis*, *Haemaphysalis flava*, *Dermacentor taiwanicus*, *Ixodes ovatus*, *Ixodes persulcatus*, and *Boophilus microplus*;

Acaridae such as *Tyrophagus putrescentiae*;

Epidermoptidae such as *Dermatophagoides farinae* and *Dermatophagoides ptrenyssnus*;

Cheyletidae such as *Cheyletus eruditus*, *Cheyletus malaccensis*, and *Cheyletus moorei*;

Dermanyssidae;

Arachnida:

Chiracanthium japonicum and *Latrodectus hasseltii*;

Chilopoda:

Thereuonema hilgendorfi and *Scolopendra subspinipes*;

Diplopoda:

Oxidus gracilis and *Nedyopus tambanus*;

Isopoda:

Armadillidium vulgare;

Gastropoda:

Limax marginatus and *Limax flavus*;

Nematoda:

Pratylenchus coffeae, *Pratylenchus fallax*, *Heterodera glycines*, *Globodera rostochiensis*, *Meloidogyne hapla*, and *Meloidogyne incognita*.

When compounds (X) are used as the active ingredients of pesticide

compositions, they may be used as such without addition of any other ingredients. However, they are usually used in admixture with solid carriers, liquid carriers and/or gaseous carriers, and if necessary, by addition of adjuvants such as surfactants, followed by formulation into various forms such emulsifiable concentrates, oil formulations, flowables, dusts, wettable powders, granules, paste formulations, microcapsule formulations, foams, aerosol formulations, carbon dioxide gas formulations, tablets, or resin formulations. These formulations may be used by processing into poison baits, shampoo, mosquito coils, electric mosquito mats, smokes, fumigants, or sheets.

In these formulations, compounds (X) are usually contained each in an amount of 0.1% to 95% by weight.

The solid carrier which can be used in the formulation may include the following materials in fine powder or granular form: clays (*e.g.*, kaolin clay, diatomaceous earth, bentonite, Fubasami clay, acid clay); talc, ceramic, and other inorganic minerals (*e.g.*, sericite, quartz, sulfur, activated carbon, calcium carbonate, hydrated silica); and chemical fertilizers (*e.g.*, ammonium sulfate, ammonium phosphate, ammonium nitrate, ammonium chloride, urea).

The liquid carrier may include aromatic or aliphatic hydrocarbons (*e.g.*, xylene, toluene, alkylnaphthalene, phenylxylylethane, kerosine, light oils, hexane, cyclohexane); halogenated hydrocarbons (*e.g.*, chlorobenzene, dichloromethane, dichloroethane, trichloroethane); alcohols (*e.g.*, methanol, ethanol, isopropyl alcohol, butanol, hexanol, ethylene glycol); ethers (*e.g.*, diethyl ether, ethylene glycol dimethyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, propylene glycol monomethyl ether, tetrahydrofuran, dioxane); esters (*e.g.*, ethyl acetate, butyl acetate); ketones (*e.g.*, acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone);

nitriles (acetonitrile, isobutyronitrile); sulfoxides (*e.g.*, dimethylsulfoxide); acid amides (*e.g.*, N,N-dimethylformamide, N,N-dimethylacetamide); vegetable oils (*e.g.*, soy bean oil and cotton seed oil); plant essential oils (*e.g.*, orange oil, hyssop oil, lemon oil); and water.

The gaseous carrier may include butane gas, Freon gas, liquefied petroleum gas (LPG), dimethyl ether, and carbon dioxide.

The surfactant may include alkyl sulfate salts; alkylsulfonic acid salts; alkylarylsulfonic acid salts; alkyl aryl ethers and their polyoxyethylene derivatives; polyethylene glycol ethers; polyol esters; and sugar alcohol derivatives.

The other adjuvants may include binders, dispersants, and stabilizers, specific examples of which are casein, gelatin, polysaccharides (*e.g.*, starch, gum arabic, cellulose derivatives, alginic acid), lignin derivatives, bentonite, sugars, synthetic water-soluble polymers (*e.g.*, polyvinyl alcohol, polyvinylpyrrolidone, polyacrylic acid), PAP (isopropyl acid phosphate), BHT (2,6-di-t-butyl-4-methylphenol), BHA (mixtures of 2-t-butyl-4-methoxyphenol and 3-t-butyl-4-methoxyphenol), vegetable oils, mineral oils, fatty acids, and fatty acid esters.

The base material for resin formulations may include vinyl chloride polymers and polyurethanes. These base materials may contain, if necessary, plasticizers such as phthalic acid esters (*e.g.*, dimethyl phthalate, dioctyl phthalate), adipic acid esters, and stearic acid. The resin formulations can be obtained by kneading the compounds into the base materials with an ordinary kneader and subsequent forming such as injection molding, extrusion, or pressing. They can be processed, if necessary, though further forming and cutting into resin formulations in various shapes such as plates, films, tapes, nets, or strings. These resin formulations are processed as, for example, collars for animals, ear tags for animals, sheet formulations, at-

tractive strings, or poles for horticultural use.

The base material for poison baits may include grain powders, vegetable oils, sugars, and crystalline cellulose. If necessary, additional agents may be added, including antioxidants such as dibutylhydroxytoluene and nordihydroguaiaretic acid; preservatives such as dehydroacetic acid; agents for preventing children and pets from erroneously eating, such as hot pepper powder; and pest-attractive flavors such as cheese flavor, onion flavor, and peanut oil.

The pesticide compositions of the present invention may be used by, for example, direct application to pests and/or application to the habitats of pests (*e.g.*, plant bodies, animal bodies, soil).

When the pesticide compositions of the present invention are used for the control of pests in agriculture and forestry, their application amounts are usually 1 to 10,000 g/ha, preferably 10 to 500 g/ha. Formulations such as emulsifiable concentrates, wettable powders, flowables, and microcapsule formulations are usually used after dilution with water to have an active ingredient concentration of 1 to 1000 ppm, while formulations such as dusts and granules are usually used as such. These formulations may be directly applied to plants to be protected from pests. These formulations can also be incorporated into soil for the control of pests inhabiting the soil, or can also be applied to beds before planting or applied to planting holes or plant bottoms in the planting. Further, the pesticide compositions of the present invention in the form of sheet formulations can be applied by the methods in which the sheet formulations are wound around plants, disposed in the vicinity of plants, or laid on the soil surface at the plant bottoms.

When the pesticide compositions of the present invention are used for the prevention of epidemics, their application amounts as active ingredient amounts are usually 0.001 to 10 mg/m^3 for spatial application or 0.001 to 100

mg/m^2 for planar application. Formulations such as emulsifiable concentrates, wettable powders, and flowables are usually applied after dilution with water to have an active ingredient concentration of 0.01 to 10,000 ppm, while formulations such as oil formulations, aerosols, smokes, or poison baits are usually applied as such.

When the pesticide compositions of the present invention are used for the control of external parasites on domestic animals such as cattle, sheep, goat, and fowl or small animals such as dogs, cats, rats, and mice, they can be used by the veterinarily well-known methods. As the specific methods of use, administration is achieved by, for example, tablets, feed incorporation, suppositories, or injections (*e.g.*, intramuscular, subcutaneous, intravenous, intraperitoneal) for systemic control, or by, for example, spraying, pour-on treatment, or spot-on treatment with an oil formulation or an aqueous solution, washing animals with a shampoo formulation, or attachment of a collar or ear tag prepared from a resin formulation to animals for non-systemic control. The amounts of compounds (X) when administered to animal bodies are usually in the range of 0.1 to 1000 mg per 1 kg weight of each animal.

The pesticide compositions of the present invention can also be used in admixture or combination with other insecticides, nematocides, acaricides, bactericides, fungicides, herbicides, plant growth regulators, synergists, fertilizers, soil conditioners, animal feeds, and the like.

Examples of the insecticides and acaricides include organophosphorus compounds such as fenitrothion [O,O-dimethyl O-(3-methyl-4-nitrophenyl) phosphorothioate], fenthion [O,O-dimethyl O-(3-methyl-4-(methythio)phenyl) phosphorothioate], diazinon [O,O-diethyl O-2-isopropyl-6-methylpyrimidin-4-yl phosphorothioate], chlorpyrifos [O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate], DDVP [2,2-dichlorovinyl dimethyl phosphate], cyanophos [O-4-cyanophenyl O,O-dimethyl phosphorothioate],

dimethoate [O,O-dimethyl S-(N-methylcarbamoylmethyl) dithiophosphate], phenthoate [ethyl 2-dimethoxyphosphinothioylthio(phenyl)acetate], malathion [diethyl (dimethoxyphosphinothioylthio)succinate], and azinphos-methyl [S-3,4-dihydro-4-oxo-1,2,3-benzotriazin-3-ylmethyl O,O-dimethyl phosphorodithioate]; carbamate compounds such as BPMC (2-sec-butylphenyl methylcarbamate), benfracarb [ethyl N-[2,3-dihydro-2,2-dimethylbenzofuran-7-yloxycarbonyl (methyl)aminothio]-N-isopropyl-β-alaninate], propoxur [2-isopropoxyphenyl N-methylcarbamate] and carbaryl [1-naphthyl N-methylcarbamate]; pyrethroid compounds such as etofenprox [2-(4-ethoxyphenyl)-2-methylpropyl-3-phenoxybenzyl ether], fenvalerate [(RS)-α-cyano-3-phenoxybenzyl (RS)-2-(4-chlorophenyl)-3-methyl-butyrate], esfenvalerate [(S)-α-cyano-3-phenoxybenzyl (S)-2-(4-chlorophenyl)-3-methylbutyrate], fenpropathrin [(RS)-α-cyano-3-phenoxybenzyl 2,2,3,3-tetramethylcyclopropanecarboxylate], cypermethrin [(RS)-α-cyano-3-phenoxybenzyl (1RS)-cis,trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate], permethrin [3-phenoxybenzyl (1RS)-cis, trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate], cyhalothrin [(RS)-α-cyano-3-phenoxybenzyl (Z)-(1RS)-cis-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate], deltamethrin [(S)-α-cyano-3-phenoxybenzyl (1R)-cis-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropane-carboxylate], cycloprothrin [(RS)-α-cyano-3-phenoxybenzyl (RS)-2,2-dichloro-1-(4-ethoxyphenyl)cyclopropanecarboxylate], fluvalinate [α-cyano-3-phenoxybenzyl N-(2-chloro-α,α,α-trifluoro-p-tolyl)-D-valinate], bifenthrin [2-methylbiphenyl-3-ylmethyl (Z)-(1RS)-cis-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate], 2-methyl-2-(4-bromodifluoro-methoxyphenyl)-propyl 3-phenoxybenzyl ether, tralomethrin [(S)-α-cyano-3-phenoxybenzyl (1R-cis)-3-{(1RS)(1,2,2,2-tetrabromoethyl)}-2,2-dimethyl-cyclopropanecarboxylate], silafluofen [(4-ethoxyphenyl){3-(4-fluoro-3-phenoxyphenyl)propyl}-

dimethylsilane], d-phenothrin [3-phenoxybenzyl (1R-cis,trans)-chrysanthemate], cyphenothrin [(RS)-α-cyano-3-phenoxybenzyl (1R-cis,trans)-chrysanthemate], d-resmethrin [5-benzyl-3-furylmethyl (1R-cis,trans)-chrysanthemate], acrinathrin [(S)-α-cyano-3-phenoxybenzyl (1R,cis(Z))-2,2-dimethyl-3-{3-oxo-3-(1,1,1,3,3,3-hexafluoropropyloxy)propenyl}cyclopropanecarboxylate], cyfluthrin [(RS)-α-cyano-4-fluoro-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate], tefluthrin [2,3,5,6-tetrafluoro-4-methylbenzyl (1RS-cis(Z))-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate], transfluthrin [2,3,5,6-tetrafluorobenzyl (1R-trans)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate], tetramethrin [3,4,5,6-tetrahydrophthalimidomethyl (1RS)-cis,trans-chrysanthemate], allethrin [(RS)-3-allyl-2-methyl-4-oxocyclopent-2-enyl (1RS)-cis,trans-chrysanthemate], prallethrin [(S)-2-methyl-4-oxo-3-(2-propynyl) cyclopent-2-enyl (1R)-cis,trans-chrysanthemate], empenthrin [(RS)-1-ethynyl-2-methyl-2-pentenyl (1R)-cis,trans-chrysanthemate], imiprothrin [2,5-dioxo-3-(prop-2-ynyl)imidazolidin-1-ylmethyl (1R)-cis,trans-2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropanecarboxylate], d-furamethrin [5-(2-propynyl) furfuryl (1R)-cis,trans-chrysanthemate] and 5-(2-propynyl)furfuryl 2,2,3,3-tetramethylcyclopropanecarboxylate; neonicotinoid derivatives such as N-cyano-N'-methyl-N'-(6-chloro-3-pyridylmethyl) acetamidine; nitenpyram [N-(6-chloro-3-pyridylmethyl)-N-ethyl-N'-methyl-2-nitrovynylidenediamine]; thiacloprid [1-(2-chloro-5-pyridylmethyl)-2-cyanoiminothiazoline]; thiamethoxam [3-((2-chloro-5-thiazolyl)methyl)-5-methyl-4-nitroiminotetrahydro-1,3,5-oxadiazine], 1-methyl-2-nitro-3-((3-tetrahydrofuryl)methyl)-guanidine and 1-(2-chloro-5-thiazolyl)methyl-3-methyl-2-nitroguanidine; nitroiminohexahydro-1,3,5-triazine derivatives; chlorinated hydrocarbons such as endosulfan [6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepine oxide], γ-BHC [1,2,3,4,5,6-hexachloro-

cyclohexane] and 1,1-bis(chlorophenyl)-2,2,2-trichloroethanol; benzoylphenylurea compounds such as chlorfluazuron [1-(3,5-dichloro-4-(3-chloro-5-trifluoromethylpyridyn-2-yloxy)phenyl)-3-(2,6-difluorobenzoyl)urea], teflubenzuron [1-(3,5-dichloro-2,4-difluorophenyl)-3-(2,6-difluorobenzoyl)urea] and flufenoxuron [1-(4-(2-chloro-4-trifluoromethylphenoxy)-2-fluorophenyl)-3-(2,6-difluorobenzoyl)urea]; juvenile hormone like compounds such as pyriproxyfen [4-phenoxyphenyl 2-(2-pyridyloxy)propyl ether], methoprene [isopropyl (2E,4E)-11-methoxy-3,7,11-trimethyl-2,4-dodecadienoate] and hydroprene [ethyl (2E,4E)-11-methoxy-3,7,11-trimethyl-2,4-dodecadienoate]; thiourea derivatives such as diafenthiuron [N-(2,6-diisopropyl-4-phenoxyphenyl)-N'-tert-butylcarbodiimide]; phenylpyrazole compounds; 4-bromo-2-(4-chlorophenyl)-1-ethoxymethyl-5-trifluoromethylpyrrol-3-carbonitrile [chlorfenapil]; metoxadiazone [5-methoxy-3-(2-methoxyphenyl)-1,3,4-oxadiazol-2(3H)-one], bromopropylate [isopropyl 4,4'-dibromobenzilate], tetradifon [4-chlorophenyl 2,4,5-trichlorophenyl sulfone], chinomethionat [S,S-6-methylquinoxaline-2,3-diyldithiocarbonate], pyridaben [2-tert-butyl-5-(4-tert-butylbenzylthio)-4-chloropyridazin-3(2H)-one], fenpyroximate [tert-butyl (E)-4-[(1,3-dimethyl-5-phenoxypyrazol-4-yl)methyleneaminooxymethyl]benzoate], tebufenpyrad [N-(4-tert-butylbenzyl)-4-chloro-3-ethyl-1-methyl-5-pyrazolecarboxamide], polynactins complex [tetranactin, dinactin and trinactin], pyrimidifen [5-chloro-N-[2-{4-(2-ethoxyethyl)-2,3-dimethylphenoxy}ethyl]-6-ethylpyrimidin-4-amine], milbemectin, abamectin, ivermectin and azadirachtin [AZAD]. Examples of the synergists include bis-(2,3,3,3-tetrachloropropyl) ether (S-421), N-(2-ethylhexyl)bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (MGK-264) and α-[2-(2-butoxyethoxy)ethoxy]-4,5-methylenedioxy-2-propyltoluene (piperonyl butoxide).

The present invention will further be illustrated by the following production examples, formulation examples, and test examples; however, the

present invention is not limited only to these examples. In the formulation examples, the compound numbers are those shown in Table 1 below.

The following will describe some production examples for compounds (X).

Production Example 1

First, 0.20 g of (4-chlorobenzyl)malononitrile was dissolved in 5 ml of N,N-dimethylformamide, to which 46 mg of sodium hydride (60% in oil) was added, while stirring under ice cooling. After the evolution of hydrogen gas ceased, while stirring under ice cooling, 0.44 ml of allyl bromide was added dropwise, followed by further stirring at room temperature overnight. Then, 10% hydrochloric acid was added to the reaction mixture, which was extracted with diethyl ether. The organic layer was successively washed with 10% hydrochloric acid, a saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, and then concentrated under reduced pressure. The residue was subjected to silica gel column chromatography to give 0.13 g of 2-allyl-2-(4-chlorobenzyl)malononitrile (compound 1).

Yield: 54%;

$n_D^{22.0}$: 1.5326.

Production Example 2

Using 0.60 g of (1-(4-chlorophenyl)-1-methylethyl)malononitrile, 10 ml of N,N-dimethylformamide, 121 mg of sodium hydride (60% in oil), and 1.20 ml of allyl bromide, and according to the process described in the Production Example 1, there was obtained 0.60 g of 2-allyl-2-(1-(4-chlorophenyl)-1-methylethyl)malononitrile (compound 2).

Yield: 85%;

$n_D^{23.5}$: 1.5354.

Production Example 3

Using 0.36 g of (1-(4-chlorophenyl)-2-methylpropyl)malononitrile, 5

ml of N,N-dimethylformamide, 75 mg of sodium hydride (60% in oil), and 0.20 ml of allyl bromide, and according to the process described in the Production Example 1, there was obtained 0.29 g of 2-allyl-2-(1-(4-chlorophenyl)-2-methylpropyl)malononitrile (compound 3).

Yield: 69%;

$n_D^{22.5}$: 1.5272.

Production Example 4

Using 0.50 g of (4-chlorobenzyl)malononitrile, 5 ml of N,N-dimethylformamide, 126 mg of sodium hydride (60% in oil), and 0.40 ml of 4-bromo-1-butene, and according to the process described in the Production Example 1, there was obtained 0.46 g of 2-(3-butenyl)-2-(4-chlorobenzyl)malononitrile (compound 4).

Yield: 72%;

m.p.: 63.7°C.

Production Example 5

Using 1.12 g of (4-(trifluoromethyl)benzyl)malononitrile, 10 ml of N,N-dimethylformamide, 0.24 g of sodium hydride (60% in oil), and 0.63 ml of allyl bromide, and according to the process described in the Production Example 1, there was obtained 0.58 g of 2-allyl-2-(4-(trifluoromethyl)benzyl)malononitrile (compound 5).

Yield: 44%;

m.p.: 80.2°C.

Production Example 6

Using 0.50 g of (4-cyanobenzyl)malononitrile, 5 ml of N,N-dimethylformamide, 132 mg of sodium hydride (60% in oil), and 0.42 ml of 4-bromo-1-butene, and according to the process described in the Production Example 1, there was obtained 0.19 g of 2-(3-butenyl)-2-(4-cyanobenzyl)malononitrile (compound 6).

Yield: 29%;

m.p.: 109.4°C.

Production Example 7

Using 0.50 g of (4-cyanobenzyl)malononitrile, 5 ml of N,N-dimethylformamide, 132 mg of sodium hydride (60% in oil), and 0.49 ml of 5-bromo-1-pentene, and according to the process described in the Production Example 1, there was obtained 0.12 g of 2-(4-cyanobenzyl)-2-(4-pentenyl)malononitrile (compound 7).

Yield: 17%;

m.p.: 91.5°C.

Production Example 8

Using 0.20 g of (2-chlorobenzyl)malononitrile, 5 ml of N,N-dimethylformamide, 46 mg of sodium hydride (60% in oil), and 0.44 ml of allyl bromide, and according to the process described in the Production Example 1, there was obtained 0.18 g of 2-allyl-2-(2-chlorobenzyl)malononitrile (compound 8).

Yield: 74%;

$n_D^{20.5}$: 1.5329.

Production Example 9

Using 0.50 g of (4-chlorobenzyl)malononitrile, 5 ml of N,N-dimethylformamide, 160 mg of sodium hydride (60% in oil), and 0.68 ml of cyclohexyl iodide, and according to the process described in the Production Example 1, there was obtained 0.20 g of 2-(4-chlorobenzyl)-2-cyclohexylmalononitrile (compound 9).

Yield: 28%;

m.p.: 107.9°C.

Production Example 10

Using 0.56 g of (1-(4-chlorophenyl)ethyl)malononitrile, 5 ml of N,N-

dimethylformamide, 160 mg of sodium hydride (60% in oil), and 0.56 ml of 4-bromo-1-butene, and according to the process described in the Production Example 1, there was obtained 0.23 g of 2-(3-butenyl)-2-(1-(4-chlorophenyl)-ethyl)malononitrile (compound 10).

Yield: 32%;

$n_D^{25.5}$: 1.5259.

Production Example 11

Using 0.50 g of (4-(trifluoromethoxy)benzyl)malononitrile, 5 ml of N,N-dimethylformamide, 123 mg of sodium hydride, and 0.35 ml of ally bromide, and according to the process described in the Production Example 1, there was obtained 0.26 g of 2-allyl-2-(4-(trifluoromethoxy)benzyl)malononitrile (compound 11).

Yield: 45%;

$n_D^{24.5}$: 1.4682.

Production Example 12

Using 0.77 g of (1-(4-(trifluoromethoxy)phenyl-2-methylpropyl)malononitrile, 5 ml of N,N-dimethylformamide, 160 mg of sodium hydride (60% in oil), and 0.55 ml of 4-bromo-1-butene, and according to the process described in the Production Example 1, there was obtained 0.30 g of 2-(3-butenyl)-2-(1-(4-(trifluoromethoxyphenyl)-2-methylpropyl)malononitrile (compound 12).

Yield: 33%;

$n_D^{25.5}$: 1.4686.

Production Example 13

Using 2.35 g of (4-bromobenzyl)malononitrile, 50 ml of N,N-dimethylformamide, 0.44 g of sodium hydride (60% in oil), and 4.23 ml of allyl bromide, and according to the process described in the Production Example 1, there was obtained 2.33 g of 2-allyl-2-(4-bromobenzyl)malononitrile (compound 13).

Yield: 85%;

m.p.: 61.7°C.

Production Example 14

Using 1.81 g of (4-cyanobenzyl)malononitrile, 50 ml of N,N-dimethylformamide, 0.44 g of sodium hydride (60% in oil), and 4.23 ml of allyl bromide, and according to the process described in the Production Example 1, there was obtained 1.04 g of 2-allyl-2-(4-cyanobenzyl)malononitrile (compound 14).

Yield: 47%;

m.p.: 81.9°C.

Production Example 15

Using 0.23 g of (4-(trifluoromethoxy)benzyl)malononitrile, 5 ml of N,N-dimethylformamide, 60 mg of sodium hydride (60% in oil), and 0.20 ml of 4-bromo-1-butene, and according to the process described in the Production Example 1, there was obtained 0.16 g of 2-(3-butenyl)-2-(4-(trifluoromethoxy)benzyl)malononitrile (compound 15).

Yield: 54%;

$n_D^{25.5}$: 1.4657.

Production Example 16

Using 0.76 g of (1-(4-(trifluoromethoxy)phenyl)ethyl)malononitrile, 5 ml of N,N-dimethylformamide, 180 mg of sodium hydride (60% in oil), and 0.61 ml of 4-bromo-1-butene, and according to the process described in the Production Example 1, there was obtained 0.36 g of 2-(3-butenyl)-2-(1-(4-(trifluoromethoxy)phenyl)ethyl)malononitrile (compound 16).

Yield: 39%;

$n_D^{25.5}$: 1.4673.

Production Example 17

Using 0.20 g of (3-chlorobenzyl)malononitrile, 5 ml of N,N-dimethyl-

formamide, 46 mg of sodium hydride (60% in oil), and 0.44 ml of allyl bromide, and according to the process described in the Production Example 1, there was obtained 0.11 g of 2-allyl-2-(3-chlorobenzyl)malononitrile (compound 17).

Yield: 45%;

$n_D^{21.5}$: 1.5302.

Production Example 18

Using 1.74 g of (4-fluorobenzyl)malononitrile, 50 ml of N,N-dimethylformamide, 0.44 g of sodium hydride (60% in oil), and 4.23 ml of allyl bromide, and according to the process described in the Production Example 1, there was obtained 2.00 g of 2-allyl-2-(4-fluorobenzyl)malononitrile (compound 18).

Yield: 93%;

$n_D^{24.5}$: 1.5028.

Production Example 19

Using 0.50 g of (4-chlorobenzyl)malononitrile, 5 ml of N,N-dimethylformamide, 0.12 g of sodium hydride (60% in oil), and 0.33 ml of isobutyl iodide, and according to the process described in the Production Example 1, there was obtained 0.42 g of 2-(4-chlorobenzyl)-2-isobutylmalononitrile (compound 19).

Yield: 65%;

m.p.: 73.2°C.

Production Example 20

Using 0.50 g of (2-methoxybenzyl)malononitrile, 10 ml of N,N-dimethylformamide, 0.12 g of sodium hydride (60% in oil), and 1.1 ml of allyl bromide, and according to the process described in the Production Example 1, there was obtained 0.50 g of 2-allyl-2-(2-methoxybenzyl)malononitrile (compound 20).

Yield: 83%;

$n_D^{18.5}$: 1.5231.

Production Example 21

Using 0.50 g of (4-chlorobenzyl)malononitrile, 5 ml of N,N-dimethylformamide, 0.126 g of sodium hydride (60% in oil), and 0.47 ml of 5-bromo-1-pentene, and according to the process described in the Production Example 1, there was obtained 0.49 g of 2-(4-chlorobenzyl)-2-(4-pentenyl)malononitrile (compound 21).

Yield: 72%;

$n_D^{22.0}$: 1.5244.

Production Example 22

Using 0.50 g of (4-chlorobenzyl)malononitrile, 5 ml of N,N-dimethylformamide, 0.126 g of sodium hydride (60% in oil), and 0.40 g of 3-chloro-1-butene, and according to the process described in the Production Example 1, there was obtained 0.35 g of 2-(4-chlorobenzyl)-2-(1-methyl-2-propenyl)-malononitrile (compound 22).

Yield: 55%;

$n_D^{22.5}$: 1.5284.

Production Example 23

Using 2.25 g of (3,4-dichlorobenzyl)malononitrile, 50 ml of N,N-dimethylformamide, 0.48 g of sodium hydride (60% in oil), and 1.30 ml of allyl bromide, and according to the process described in the Production Example 1, there was obtained 1.96 g of 2-allyl-2-(3,4-dichlorobenzyl)malononitrile (compound 23).

Yield: 74%;

m.p.: 71.8°C.

Production Example 24

Using 1.13 g of (2,4-dichlorobenzyl)malononitrile, 20 ml of N,N-di-

methylformamide, 0.24 g of sodium hydride (60% in oil), and 0.63 ml of allyl bromide, and according to the process described in the Production Example 1, there was obtained 0.78 g of 2-allyl-2-(2,4-dichlorobenzyl)malononitrile (compound 24).

Yield: 59%;

$n_D^{24.5}$: 1.5447

Production Example 25

Using 0.50 g of (4-chlorobenzyl)malononitrile, 5 ml of N,N-dimethylformamide, 0.16 g of sodium hydride (60% in oil), and 0.60 ml of 1-bromo-3-methyl-2-butene, and according to the process described in the Production Example 1, there was obtained 0.52 g of 2-(4-chlorobenzyl)-2-(3-methyl-2-butenyl)malononitrile (compound 25).

Yield: 77%;

$n_D^{25.5}$: 1.5263.

Production Example 26

Using 0.80 g of (1-(4-chlorophenyl)-2-methylpropyl)malononitrile, 10 ml of N,N-dimethylformamide, 0.21 g of sodium hydride (60% in oil), and 0.70 ml of 4-bromo-1-butene, and according to the process described in Production Example 1, there was obtained 0.32 g of 2-(3-butenyl)-2-(1-(4-chlorophenyl)-2-methylpropyl)malononitrile (compound 26).

Yield: 32%;

$n_D^{25.5}$: 1.5217.

Production Example 27

Using 0.20 g of (4-(trifluoromethoxy)benzyl)malononitrile, 5 ml of N,N-dimethylformamide, 50 mg of sodium hydride (60% in oil), and 0.19 ml of 1-bromo-3-methyl-2-butene, and according to the process described in Production Example 1, there was obtained 0.19 g of 2-(3-methyl-2-butenyl)-2-(4-(trifluoromethoxy)benzyl)malononitrile (compound 27).

Yield: 74%;

$n_D^{24.5}$: 1.4707.

Production Example 28

Using 0.50 g of (3-methoxybenzyl)malononitrile, 10 ml of N,N-dimethylformamide, 0.12 g of sodium hydride (60% in oil), and 1.1 ml of allyl bromide, and according to the process described in the Production Example 1, there was obtained 0.45 g of 2-allyl-2-(3-methoxybenzyl)malononitrile (compound 28).

Yield: 74%;

$n_D^{22.0}$: 1.5238.

Production Example 29

Using 0.50 g of (4-methoxybenzyl)malononitrile, 10 ml of N,N-dimethylformamide, 0.12 g of sodium hydride (60% in oil), and 1.1 ml of allyl bromide, and according to the process described in the Production Example 1, there was obtained 0.50 g of 2-allyl-2-(4-methoxybenzyl)malononitrile (compound 29).

Yield: 83%;

$n_D^{22.0}$: 1.5252.

Production Example 30

First, 0.24 g of (4-(trifluoromethoxy)benzylidene)malononitrile, 0.66 g of allyltributyltin, and 0.71 g of methyl iodide were dissolved in 10 ml of benzene, and the solution was heated to the reflux temperature. Then, 40 mg of azobis(isobutyronitrile) was added, and the mixture was stirred for 13 hours, while heating under reflux. The reaction mixture is poured into a mixture of 40 ml of hexane and 40 ml of acetonitrile, followed by phase separation. The acetonitrile layer was concentrated, and the resulting residue was subjected to silica gel thin layer chromatography to give 0.19 g of 2-allyl-2-(1-(4-(trifluoromethoxy)phenyl)ethyl)malononitrile (compound 30).

Yield: 65%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.68 (3H, d), 2.42-2.61 (2H, m), 3.25 (1H, q), 5.23-5.44 (2H, m), 5.83-5.94 (1H, m), 7.25 (2H, d), 7.40 (2H, d).

Production Example 31

Using 0.24 g of (4-(trifluoromethoxy)benzylidene)malononitrile, 10 ml of benzene, 0.66 g of allyltributyltin, 0.89 g of chloroiodomethane, and 66 mg of azobis(isobutyronitrile), and according to the process described in Production Example 30, there was obtained 0.20 g of 2-allyl-2-(1-(4-(trifluoromethoxy)phenyl)-2-chloroethyl)malononitrile (compound 31).

Yield: 61%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.43-2.60 (2H, m), 3.43 (1H, dd), 4.03 (1H, dd), 4.22 (1H, dd), 5.33-5.53 (2H, m), 5.78-6.01 (1H, m), 7.35 (2H, m), 7.41 (2H, m).

Production Example 32

Using 0.50 g of (1-(4-(trifluoromethoxy)phenyl)-2-propenyl)malononitrile, 4 ml of N,N-dimethylformamide, 83 mg of sodium hydride (60% in oil), and 0.51 g of 4-bromo-1-butene, and according to the process described in Production Example 1, there was obtained 0.56 g of 2-(3-butenyl)-2-(1-(4-(trifluoromethoxy)phenyl)-2-propenyl)malononitrile (compound 32).

Yield: 93%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.77-2.08 (2H, m), 2.41-2.51 (2H, m), 3.67 (1H, d), 5.07-5.18 (2H, m), 5.37-5.51 (2H, m), 5.69-5.82 (1H, m), 5.19-5.33 (1H, m), 7.26 (2H, m), 7.45 (2H, m).

Production Example 33

Using 0.25 g of (1-(4-(trifluoromethoxy)phenyl)-2-propenyl)malononitrile, 2 ml of N,N-dimethylformamide, 42 mg of sodium hydride (60% in oil), and 0.45 g of allyl bromide, and according to the process described in Production Example 1, there was obtained 0.25 g of 2-allyl-2-(1-(4-(trifluoro-

methoxy)phenyl)-2-propenyl)malononitrile (compound 33).

Yield: 87%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.50-2.73 (2H, m), 3.68 (1H, d), 5.34-5.52 (4H, m), 5.83-5.97 (1H, m), 6.18-6.33 (1H, m), 7.27 (2H, m), 7.46 (2H, m).

Production Example 34

Using 0.62 g of (1-(4-(trifluoromethoxy)phenyl)-2-propenyl)malononitrile, 5 ml of N,N-dimethylformamide, 103 mg of sodium hydride (60% in oil), and 0.56 g of 3-bromo-1-propyne, and according to the process described in Production Example 1, there was obtained 0.59 g of 2-(2-propynyl)-2-(1-(4-(trifluoromethoxy)phenyl)-2-propenyl)malononitrile (compound 34).

Yield: 83%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.47 (1H, t), 2.74-2.93 (2H, m), 3.96 (1H, d), 5.47-5.55 (2H, m), 6.19-6.31 (1H, m), 7.28 (2H, m), 7.49 (2H, m).

Production Example 35

First, 0.41 g of 2-(3-butenyl)-2-(4-hydroxybenzyl)malononitrile and 0.76 g of dibromodifluoromethane was dissolved in 5 ml of N,N-dimethylformamide, and while stirring under ice-cooling, 80 mg of sodium hydride (60% in oil) was added, and the mixture was heated to 80 °C, followed by stirred for 5 hours. Then, a saturated ammonium chloride aqueous solution was added to the reaction mixture, which was extracted diethyl ether. The organic layer was successively washed with water, a saturated sodium chloride aqueous solution, dried over anhydrous magnesium sulfate, and then concentrated under reduced pressure. The residue was subjected to silica gel column chromatography to give 0.16 g of 2-(3-butenyl)-2-(4-(bromodifluoromethoxy)benzyl)malononitrile (compound 35) as a low-polar compound.

Yield: 25%;

m.p.: 50.2°C.

Also given was 58mg of 2-(3-butenyl)-2-(4-(difluoromethoxy)benzyl)-malononitrile (compound 36) as a high-polar compound.

Yield: 12%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.02-2.07(2H, m), 2.44-2.52(2H, m), 3.21(2H, s), 5.11-5.20(2H, m), 5.77-5.86(1H, m), 6.54(1H, t), 7.16(2H, d), 7.38(2H, m).

Production Example 36

Using 0.43 g of (3,4-(methylenedioxy)benzyl)malononitrile, 5 ml of N,N-dimethylformamide, 100 mg of sodium hydride (60% in oil), and 0.36 g of 4-bromo-1-butene, and according to the process described in Production Example 1, there was obtained 0.42 g of 2-(3-butenyl)-2-(3,4-(methylenedioxy)benzyl)malononitrile (compound 37).

Yield: 76%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.99-2.05 (2H, m), 2.45-2.48 (2H, m), 3.14 (2H, s), 5.09-5.20 (2H, m), 5.72-5.90 (1H, m), 6.00 (2H, s), 6.82-6.85 (3H, m).

Production Example 37

First, 0.30 g of 2-(3-butenyl)-2-(4-hydroxybenzyl)malononitrile and 0.19 g of allyl bromide was dissolved in 5 ml of N,N-dimethylformamide, and 0.22 g of potassium carbonate was added, followed by stirred overnight at room temperature. Then, water was added to the reaction mixture, which was extracted diethyl ether. The organic layer was successively washed with water, a saturated sodium chloride aqueous solution, dried over anhydrous magnesium sulfate, and then concentrated under reduced pressure. The residue was subjected to silica gel column chromatography to give 0.34 g of 2-(3-butenyl)-2-(4-(2-propenyloxy)benzyl)malononitrile (compound 38).

Yield: 96%;

m.p.: 77.7°C.

Production Example 38

First, 0.48 g of 4-(trifluoromethoxy)benzylidenemalononitrile, 0.10 g of tetrakis(triphenylphosphine)palladium, and 0.26 g of allylmethyl carbonate were dissolved in 20 ml of tetrahydrofuran, and the solution was stirred at room temperature for 10 hours. Then, the residue obtained by concentration under reduced pressure was subjected to silica gel chromatography to give 0.56 g of 2-allyl-2-(4-(trifluoromethoxy)-α-methoxybenzyl)malononitrile (compound 39).

Yield: 89%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.66-2.79 (2H, m), 3.36 (3H, s), 4.43 (1H, s), 5.38-5.46 (2H, m), 5.85-5.99 (1H, m), 7.32 (2H, d), 7.53 (2H, d).

Production Example 39

Using 0.50 g of (4-(trifluoromethylthio)benzyl)malononitrile, 6 ml of N,N-dimethylformamide, 90 mg of sodium hydride (60% in oil), and 0.29 g of allyl bromide, and according to the process described in Production Example 1, there was obtained 0.49 g of 2-allyl-2-(4-(trifluoromethylthio)benzyl)-malononitrile (compound 41).

Yield: 84%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.69-2.75 (2H, m), 3.21 (2H, s), 5.39-5.51 (2H, m), 5.88-6.02 (1H, m), 7.45 (2H, d), 7.70 (2H, d).

Production Example 40

Using 0.50 g of (4-(trifluoromethylthio)benzyl)malononitrile, 6 ml of N,N-dimethylformamide, 90 mg of sodium hydride (60% in oil), and 0.32 g of 4-bromo-1-butene, and according to the process described in Production Example 1, there was obtained 0.26 g of 2-(3-butenyl)-2-(4-(trifluoromethylthio)benzyl)malononitrile (compound 42).

Yield: 44%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.04-2.10 (2H, m), 2.45-2.54 (2H, m), 3.25 (2H, s), 5.10-5.22 (2H, m), 5.74-5.87 (1H, m), 7.45 (2H, d), 7.71 (2H, m).

Production Example 41

Using 0.51 g of 4-(trifluoromethylthio)benzylidenemalononitrile, 0.10 g of tetrakis(triphenylphosphine)palladium, 0.26 g of allylmethyl carbonate, and 20 ml of tetrahydrofuran, and according to the process described in Production Example 38, there was obtained 0.49 g of 2-allyl-2-(4-(trifluoromethylthio)-α-methoxybenzyl)malononitrile (compound 43).

Yield: 75%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.72-2.76 (2H, m), 3.38 (3H, s), 4.46 (1H, s), 5.38-5.48 (2H, m), 5.79-5.94 (1H, m), 7.56 (2H, m), 7.76 (2H, m).

Production Example 42

Using 1.76 g of (4-ethoxybenzyl)malononitrile, 30 ml of N,N-dimethylformamide, 0.40 g of sodium hydride (60% in oil), and 4.2 ml of allyl bromide, and according to the process described in the Production Example 1, there was obtained 1.30 g of 2-allyl-2-(4-ethoxybenzyl)malononitrile (compound 44).

Yield: 54%;

m.p.: 84.3°C.

Production Example 43

Using 0.50 g of (4-(trifluoromethoxy)benzyl)malononitrile, 6 ml of N,N-dimethylformamide, 95 mg of sodium hydride (60% in oil), and 0.47 g of isopentyl bromide, and according to the process described in Production Example 1, there was obtained 0.42 g of 2-(3-methylbutyl)-2-(4-(trifluoromethoxy)benzyl)malononitrile (compound 45).

Yield: 65%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 0.96 (3H, d), 1.59-1.65 (3H, m), 1.94-2.01 (2H, m), 3.20 (2H, s), 7.26 (2H, d), 7.43 (2H, d).

Production Example 44

Using 0.50 g of (4-(trifluoromethylthio)benzyl)malononitrile, 6 ml of N,N-dimethylformamide, 90 mg of sodium hydride (60% in oil), and 0.21 g of 1-chloro-2-butene, and according to the process described in Production Example 1, there was obtained 0.40 g of 2-(2-butenyl)-2-(4-(trifluoromethylthio)benzyl)malononitrile (compound 46).

Yield: 66%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.72 (3H, dd, Z), 1.80 (3H, dd, E), 2.68 (2H, d, E), 2.73 (2H, d, Z), 3.18 (2H, s, Z), 3.19 (2H, s, E), 5.49-5.68 (1H, m, E, Z), 5.78-6.00 (1H, m, E, Z),7.45 (2H, d, E, Z), 7.70 (2H, d, E, Z).

Production Example 45

Using 0.50 g of (4-(trifluoromethylthio)benzyl)malononitrile, 6 ml of N,N-dimethylformamide, 90 mg of sodium hydride (60% in oil), and 0.21 g of 3-chloro-1-butene, and according to the process described in Production Example 1, there was obtained 0.14 g of 2-(1-methyl-2-propenyl)-2-(4-(trifluoromethylthio)benzyl)malononitrile (compound 47).

Yield: 24%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.47 (3H, d), 2.62-2.74 (1H, m), 3.19 (2H, dd), 5.35-5.46 (2H, m), 5.80-5.95 (2H, m), 7.45 (2H, d), 7.69 (2H, d).

Production Example 46

Using 1.93 g of (1-(3-chlorophenyl)-1-methylethyl)malononitrile, 30 ml of N,N-dimethylformamide, 0.39 g of sodium hydride (60% in oil), and 3.70 ml of allyl bromide, and according to the process described in the Production Example 1, there was obtained 1.14 g of 2-allyl-2-(1-(3-chlorophenyl)-1-methylethyl)malononitrile (compound 48).

Yield: 50%;

m.p.: 84.3°C.

Production Example 47

Using 0.60 g of (1-(2-chlorophenyl)-1-methylethyl)malononitrile, 10 ml of N,N-dimethylformamide, 0.12 g of sodium hydride (60% in oil), and 1.2 ml of allyl bromide, and according to the process described in the Production Example 1, there was obtained 0.60 g of 2-allyl-2-(1-(2-chlorophenyl)-1-methylethyl)malononitrile (compound 49).

Yield: 71%;

$n_D^{23.5}$: 1.5398.

Production Example 48

Using 2.01 g of (4-nitrobenzyl)malononitrile, 50 ml of N,N-dimethylformamide, 0.44 g of sodium hydride (60% in oil), and 4.23 ml of allyl bromide, and according to the process described in the Production Example 1, there was obtained 1.13 g of 2-allyl-2-(4-nitrobenzyl)malononitrile (compound 50).

Yield: 47%;

m.p.: 94.2°C.

Production Example 49

Using 0.50 g of (4-chlorobenzyl)malononitrile, 5 ml of N,N-dimethylformamide, 0.12 g of sodium hydride (60% in oil), and 0.27 ml of isopropyl iodide, and according to the process described in the Production Example 1, there was obtained 0.19 g of 2-(4-chlorobenzyl)-2-isopropylmalononitrile (compound 51).

Yield: 31%;

$n_D^{22.5}$: 1.5229.

Production Example 50

Using 0.50 g of (4-(trifluoromethyl)benzyl)malononitrile, 21 ml of N,N-dimethylformamide, 100 mg of sodium hydride (60% in oil), and 0.45 g of 4-bromo-1-butene, and according to the process described in Production Example 1, there was obtained 0.25 g of 2-(3-butenyl)-2-(4-(trifluoromethyl)-

benzyl)malononitrile (compound 52).

Yield: 20%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.05-2.10 (2H, m), 2.46-2.52 (2H, m), 3.28 (2H, s), 5.12-5.22 (2H, m), 5.77-5.86 (1H, m), 7.52 (2H, d), 7.69 (2H, d).

Production Example 51

Using 2.25 g of (2,3-dichlorobenzyl)malononitrile, 20 ml of N,N-dimethylformamide, 0.48 g of sodium hydride (60% in oil), and 1.30 ml of allyl bromide, and according to the process described in the Production Example 1, there was obtained 1.72 g of 2-allyl-2-(2,3-dichlorobenzyl)-malononitrile (compound 53).

Yield: 65%;

$n_D^{23.5}$: 1.5448.

Production Example 52

Using 2.25 g of (2,6-dichlorobenzyl)malononitrile, 20 ml of N,N-dimethylformamide, 0.48 g of sodium hydride (60% in oil), and 1.30 ml of allyl bromide, and according to the process described in the Production Example 1, there was obtained 2.00 g of 2-allyl-2-(2,6-dichlorobenzyl)malononitrile (compound 54).

Yield: 75%;

$n_D^{23.5}$: 1.5483.

Production Example 53

First, 0.50 g of 4-(trifluoromethylthio)benzylidenemalononitrile, 60 mg of tris(dibenzylideneacetone)dipalladium-chloroform complex, and 0.11 g of 1,1'-bis(diphenylphosphino)ferrocene were added to 10 ml of tetrahydrofuran, and 0.30 g of allyl chloride and 0.39 g of trimethylsilyl cyanide were further added under an atmosphere of nitrogen, followed by stirring at 75°C for a day. The reaction mixture was then filtered through silica gel and the filtrate was concentrated. The residue was subjected to silica gel chroma-

tography to give 0.42 g of 2-allyl-2-(4-(trifluoromethylthio)-α-cyanobenzyl)-malononitrile (compound 56).

Yield: 67%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.92-3.12 (2H, m), 4.29 (1H, s), 5.59-5.65 (2H, m), 5.81-5.98 (1H, m), 7.63 (2H, d), 7.82 (2H, d).

Production Example 54

Using 0.47 g of 4-(trifluoromethoxy)benzylidenemalononitrile, 60 mg of tris(dibenzylideneacetone)dipalladium-chloroform complex, 0.11 g of 1,1'-bis(diphenylphosphino)ferrocene, 10 ml of tetrahydrofuran, 0.30 g of allyl chloride, and 0.39 g of trimethylsilyl cyanide, and according to the process described in Production Example 53, there was obtained 0.42 g of 2-allyl-2-(4-(trifluoromethoxy)-α-cyanobenzyl)malononitrile (compound 55).

Yield: 70%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.92-3.10 (2H, m), 4.27 (1H, s), 5.58-5.63 (2H, m), 5.91-5.97 (1H, m), 7.37 (2H, d), 7.62 (2H, d).

Production Example 55

Using 0.30 g of allylmalononitrile, 4 ml of N,N-dimethylformamide, 130 mg of sodium hydride (60% in oil), and 0.99 g of 2,4-bis(trifluoromethyl)-benzyl bromide, and according to the process described in Production Example 1, there was obtained 0.70 g of 2-allyl-2-(2,4-bis(trifluoromethyl)benzyl)-malononitrile (compound 57).

Yield: 72%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.82 (2H, d), 3.47 (2H, s), 5.45-5.58 (2H, m), 5.89-6.05 (1H, m), 7.92 (1H, d), 7.98 (1H, d), 8.02 (1H, s).

Production Example 56

Using 0.30 g of allylmalononitrile, 4 ml of N,N-dimethylformamide, 125 mg of sodium hydride (60% in oil), and 0.85 g of 2-chloro-4-(trifluoromethyl)benzyl bromide, and according to the process described in Production

Example 1, there was obtained 0.40 g of 2-allyl-2-(2-chloro-4-(trifluoromethyl)benzyl)malononitrile (compound 58).

Yield: 47%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.84 (2H, d), 3.51 (2H, s), 5.41-5.56 (2H, m), 5.88-6.07 (1H, m), 7.62 (1H, d), 7.71 (1H, d), 7.83 (1H, s).

Production Example 57

Using 0.50 g of (4-(trifluoromethoxy)benzyl)malononitrile, 3 ml of N,N-dimethylformamide, 93 mg of sodium hydride (60% in oil), and 0.42 g of 1-bromo-2-butyne, and according to the process described in Production Example 1, there was obtained 0.47 g of 2-(2-butynyl)-2-(4-(trifluoromethoxy)-benzyl)malononitrile (compound 59).

Yield: 70%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.93 (3H, t), 2.85 (2H, q), 3.33 (2H, s), 7.25 (2H, d), 7.45 (2H, d).

Production Example 58

Using 0.30 g of (3-butenyl)malononitrile, 5 ml of N,N-dimethylformamide, 110 mg of sodium hydride (60% in oil), and 0.75 g of 2-chloro-4-(trifluoromethyl)benzyl bromide, and according to the process described in Production Example 1, there was obtained 0.30 g of 2-(3-butenyl)-2-(2-chloro-4-(trifluoromethyl)benzyl)malononitrile (compound 60).

Yield: 39%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.10-2.17 (2H, m), 2.49-2.52 (2H, m), 3.53 (2H, s), 5.11-5.22 (2H, m), 5.72-5.88 (1H, m), 7.62 (1H, d), 7.70 (1H, d), 7.75 (1H, s).

Production Example 59

Using 0.60 g of allylmalononitrile, 8 ml of N,N-dimethylformamide, 255 mg of sodium hydride (60% in oil), and 1.55 g of 4-(methylsulfonyl)benzyl bromide, and according to the process described in Production Example 1,

there was obtained 0.64 g of 2-allyl-2-(4-(methylsulfonyl)benzyl)malononitrile (compound 61).

Yield: 41%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.78 (2H, d), 3.10 (3H, s), 3.29 (2H, s), 5.45-5.53 (2H, m), 5.88-6.07 (1H, m), 7.61 (2H, d), 8.01 (2H, d).

Production Example 60

Using 1.23 g of (2,3,4,5,6-pentafluorobenzyl)malononitrile, 20 ml of N,N-dimethylformamide, 0.24 g of sodium hydride (60% in oil), and 0.63 ml of allyl bromide, and according to the process described in the Production Example 1, there was obtained 0.98 g of 2-allyl-2-(2,3,4,5,6-pentafluorobenzyl)malononitrile (compound 62).

Yield: 68%;

m.p.: 78.2°C.

Production Example 61

Using 0.15 g of allylmalononitrile, 5 ml of N,N-dimethylformamide, 62 mg of sodium hydride (60% in oil), and 0.43 g of 2-nitro-4-(trifluoromethyl)benzyl bromide, and according to the process described in Production Example 1, there was obtained 0.32 g of 2-allyl-2-(2-nitro-4-(trifluoromethyl)benzyl)malononitrile (compound 63).

Yield: 70%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.88 (2H, d), 3.80 (2H, s), 5.46-5.57 (2H, m), 5.88-6.05 (1H, m), 7.82 (1H, d), 7.94 (1H, d), 8.46 (1H, s).

Production Example 62

Using 0.15 g of allylmalononitrile, 5 ml of N,N-dimethylformamide, 62 mg of sodium hydride (60% in oil), and 0.44 g of 2,6-dichloro-4-(trifluoromethyl)benzyl bromide, and according to the process described in Production Example 1, there was obtained 0.20 g of 2-allyl-2-(2,6-dichloro-4-(trifluoromethyl)benzyl)malononitrile (compound 64).

Yield: 43%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.94 (2H, d), 3.75 (1H, s), 5.50-5.58 (2H, m), 5.95-6.10 (1H, s), 7.71 (2H, s).

Production Example 63

Using 0.15 g of (3-butenyl)malononitrile, 5 ml of N,N-dimethylformamide, 55 mg of sodium hydride (60% in oil), and 0.39 g of 2,6-dichloro-4-(trifluoromethyl)benzyl bromide, and according to the process described in Production Example 1, there was obtained 95 mg of 2-(3-butenyl)-2-(2,6-dichloro-4-(trifluoromethyl)benzyl)malononitrile (compound 65).

Yield: 22%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.22-2.28 (2H, m), 2.49-2.57 (2H, m), 3.77 (2H, s), 5.13-5.23 (2H, m), 5.78-5.90 (1H, m), 7.69 (2H, s).

Production Example 64

Using 0.41 g of (1-(3-chlorophenyl)-2-methylpropyl)malononitrile, 5 ml of N,N-dimethylformamide, 85 mg of sodium hydride (60% in oil), and 0.22 ml of allyl bromide, and according to the process described in the Production Example 1, there was obtained 0.35 g of 2-allyl-2-(1-(3-chlorophenyl)-2-methylpropyl)malononitrile (compound 66).

Yield: 73%;

$n_D^{23.0}$: 1.5267.

Production Example 65

Using 97 mg of (3-butenyl)malononitrile, 5 ml of N,N-dimethylformamide, 37 mg of sodium hydride (60% in oil), and 0.25 g of 2-nitro-4-(trifluoromethyl)benzyl bromide, and according to the process described in Production Example 1, there was obtained 0.12 g of 2-(3-butenyl)-2-(2-nitro-4-(trifluoromethyl)benzyl)malononitrile (compound 67).

Yield: 43%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.21-2.29 (2H, m), 2.54-2.65 (2H, m),

5.64-5.76 (2H, m), 5.82-5.98 (1H, m), 7.33 (1H, d), 8.03 (1H, m), 8.45 (1H, s).

Production Example 66

Using 0.50 g of (4-chlorobenzyl)malononitrile, 5 ml of N,N-dimethylformamide, 0.16 g of sodium hydride (60% in oil), and 0.33 ml of methyl iodide, and according to the process described in the Production Example 1, there was obtained 0.23 g of 2-(4-chlorobenzyl)-2-methylmalononitrile (compound 68).

Yield: 43%;

m.p.: 91.1°C.

Production Example 67

Using 0.30 g of allylmalononitrile, 4 ml of N,N-dimethylformamide, 124 mg of sodium hydride (60% in oil), and 0.80 g of 3-fluoro-4-(trifluoromethyl)benzyl bromide, and according to the process described in Production Example 1, there was obtained 0.37 g of 2-allyl-2-(3-fluoro-4-(trifluoromethyl)benzyl)malononitrile (compound 69).

Yield: 46%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.77 (2H, d), 3.23 (2H, s), 5.43-5.54 (2H, m), 5.86-5.98 (1H, m), 7.25 (1H, m), 7.29 (1H, d), 7.65-7.72 (1H, m).

Production Example 68

Using 0.30 g of allylmalononitrile, 6 ml of N,N-dimethylformamide, 124 mg of sodium hydride (60% in oil), and 0.68 g of 4-(methylthio)benzyl bromide, and according to the process described in Production Example 1, there was obtained 0.42 g of 2-allyl-2-(4-(methylthio)benzyl)malononitrile (compound 70).

Yield: 62%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.49 (3H, s), 2.70 (2H, s), 3.16 (2H, s), 5.38-5.47 (2H, m), 5.80-5.99 (1H, m), 7.27 (2H, d), 7.28 (2H, d).

Production Example 69

Using 0.50 g of (4-(trifluoromethyl)benzyl)malononitrile, 6 ml of N,N-dimethylformamide, 98 mg of sodium hydride (60% in oil), and 0.41 g of 1-iodopropane, and according to the process described in Production Example 1, there was obtained 0.21 g of 2-propyl-2-(4-(trifluoromethyl)benzyl)-malononitrile (compound 71).

Yield: 41%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.06 (3H, t), 1.68-1.77 (2H, m), 1.88-1.96 (2H, m), 7.48 (2H, d), 7.63 (2H, m).

Production Example 70

Using 0.50 g of (4-chlorobenzyl)malononitrile, 5 ml of N,N-dimethylformamide, 0.16 g of sodium hydride (60% in oil), and 0.39 ml of ethyl bromide, and according to the process described in the Production Example 1, there was obtained 0.20 g of 2-(4-chlorobenzyl)-2-ethylmalononitrile (compound 72).

Yield: 35%;

m.p.: 70.9°C.

Production Example 71

Using 0.50 g of (4-chlorobenzyl)malononitrile, 5 ml of N,N-dimethylformamide, 0.16 g of sodium hydride (60% in oil), and 0.85 g of (Z)-1-bromo-3-hexene, and according to the process described in the Production Example 1, there was obtained 0.22 g of 2-(4-chlorobenzyl)-2-((Z)-3-hexenyl)malononitrile (compound 73).

Yield: 31%;

m.p.: 44.8°C.

Production Example 72

Using 0.56 g of (1-(4-chlorophenyl)ethyl)malononitrile, 5 ml of N,N-dimethylformamide, 160 mg of sodium hydride (60% in oil), and 0.46 ml of allyl bromide, and according to the process described in the Production

Example 1, there was obtained 0.29 g of 2-allyl-2-(1-(4-chlorophenyl)ethyl)-malononitrile (compound 74).

Yield: 43%;

$n_D^{25.5}$: 1.5294.

Production Example 73

Using 0.50 g of (4-(trifluoromethyl)benzyl)malononitrile, 6 ml of N,N-dimethylformamide, 98 mg of sodium hydride (60% in oil), and 0.27 g of bromoethane, and according to the process described in Production Example 1, there was obtained 0.33 g of 2-ethyl-2-(4-(trifluoromethyl)benzyl)malononitrile (compound 75).

Yield: 58%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.35 (2H, t), 2.06 (2H, q), 3.26 (2H, s), 7.52 (2H, d), 7.68 (2H, d).

Production Example 74

Using 0.56 g of (1-(4-chlorophenyl)ethyl)malononitrile, 5 ml of N,N-dimethylformamide, 160 mg of sodium hydride (60% in oil), and 0.65 ml of 1-bromo-4-pentene, and according to the process described in the Production Example 1, there was obtained 0.25 g of 2-(1-(4-chlorophenyl)ethyl)-2-(4-pentenyl)malononitrile (compound 76).

Yield: 33%;

$n_D^{25.5}$: 1.5204.

Production Example 75

Using 0.50 g of (4-methylbenzyl)malononitrile, 5 ml of N,N-dimethylformamide, 0.18 g of sodium hydride (60% in oil), and 0.50 ml of allyl bromide, and according to the process described in the Production Example 1, there was obtained 0.37 g of 2-allyl-2-(4-methylbenzyl)malononitrile (compound 77).

Yield: 60%;

m.p.: 74.5°C.

Production Example 76

First, 0.40 g of 2-(3-butenyl)-2-(4-hydroxybenzyl)malononitrile and 0.22 g of acetic anhydride was dissolved in 5 ml of toluene, to which 0.23 g of triethylamine was added, followed by stirring overnight at room temperature. Then, water was added to the reaction mixture, which was extracted with diethyl ether. The organic layer was successively washed with a saturated ammonium chloride aqueous solution, a saturated sodium bicarbonate aqueous solution, a saturated sodium chloride aqueous solution, dried over anhydrous magnesium sulfate, and then concentrated under reduced pressure. The residue was subjected to silica gel column chromatography to give 0.45 g of 2-(3-butenyl)-2-(4-(acetyloxy)benzyl)malononitrile (compound 78).

Yield: 95%;

m.p.: 80.2°C.

Production Example 77

Using 0.50 g of (4-(trifluoromethyl)benzyl)malononitrile, 10 ml of N,N-dimethylformamide, 89 mg of sodium hydride (60% in oil), and 0.33 g of 5-bromo-1-pentene, and according to the process described in Production Example 1, there was obtained 0.16 g of 2-(4-pentenyl)-2-(4-(trifluoromethyl)-benzyl)malononitrile (compound 79).

Yield: 25%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.84-1.87 (2H, m), 1.96-2.02 (2H, m), 2.18 (2H, t), 3.25 (2H, s), 5.05-5.11 (2H, m), 5.76-5.86 (1H, m), 7.51 (2H, d), 7.58 (2H, d).

Production Example 78

First, 0.40 g of 2-(3-butenyl)-2-(4-hydroxybenzyl)malononitrile was dissolved in 5 ml of N,N-dimethylformamide, to which 75 mg of sodium

hydride (60% in oil) was added, while stirring under ice cooling. After the evolution of hydrogen gas ceased, while stirring under ice cooling, 0.49 g of 1,1,2,2-tetrafluoro-1-iodoethane was added dropwise, followed by further stirring at room temperature overnight. Then, a saturated ammonium chloride aqueous solution was added to the reaction mixture, which was extracted with diethyl ether. The organic layer was successively washed with water, a saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, and then concentrated under reduced pressure. The residue was subjected to silica gel column chromatography to give 82 mg of 2-(3-butenyl)-2-(4-(1,1,2,2-tetrafluoroethoxy)benzyl)malononitrile (compound 80).

Yield: 14%;

m.p.: 60.5°C.

Production Example 79

Using 0.40 g of 2-(3-butenyl)-2-(4-hydroxybenzyl)malononitrile, 5 ml of N,N-dimethylformamide, 75 mg of sodium hydride (60% in oil), and 0.45 g of 2,2,2-trifluoro-1-iodoethane, and according to the process described in the Production Example 78, there was obtained 70 mg of 2-(3-butenyl)-2-(4-(2,2,2-trifluoroethoxy)benzyl)malononitrile (compound 81).

Yield: 13%;

m.p.: 58.0°C.

Production Example 80

First, 0.48 g of (4-(trifluoromethoxy)benzyliden)malononitrile and 1.0 g of ethanol was dissolved in 20 ml of tetrahydrofuran, to which 0.10 g of tetrakis(triphenylphosphine)palladium and 0.26 g of allyl methyl carbonate was added, followed by further stirring for 10 hours at room temperature. Then, the reaction mixture was concentrated under reduced pressure. The residue was subjected to silica gel column chromatography to give 0.65 g of

2-allyl-2-(4-(trifluoromethoxy)-α-ethoxybenzyl)malononitrile (compound 82).

Yield: 99%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.26(3H, t), 2.66-2.79(2H, m), 3.36-3.57(2H, m), 4.54(1H, s), 5.38-5.46(2H, m), 5.87-5.99(1H, m), 7.30(2H, d), 7.55(2H, d).

Production Example 81

Using 0.36 g of (4-cyanobenzyliden)malononitrile, 0.10 g of tetrakis(triphenylphosphine)palladium, and 0.26 g of allyl methyl carbonate, and 20 ml of tetrahydrofuran, and according to the process described in the Production Example 38, there was obtained 0.11 g of 2-allyl-2-(4-cyano-α-methoxybenzyl)malononitrile (compound 83).

Yield: 22%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.72-2.81(2H, m), 3.38(3H, s), 4.47(1H, s), 5.39-5.49(2H, m), 5.80-5.98(1H, m), 7.64(2H, d), 7.79(2H, d).

Production Example 82

Using 0.38 g of (4-chlorobenzyliden)malononitrile, 0.10 g of tetrakis(triphenylphosphine)palladium, and 0.26 g of allyl methyl carbonate, and 20 ml of tetrahydrofuran, and according to the process described in the Production Example 38, there was obtained 0.44 g of 2-allyl-2-(4-chloro-α-methoxybenzyl)malononitrile (compound 84).

Yield: 84%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.65-2.76(2H, m), 3.35(3H, s), 4.41(1H, s), 5.37-5.47(2H, m), 5.85-6.00(1H, m), 7.45(4H, bs).

Production Example 83

Using 0.41 g of (2,2-dimethylpropyl)malononitrile, 7 ml of N,N-dimethylformamide, 0.13 g of sodium hydride (60% in oil), and 0.92 g of 4-(trifluoromethyl)benzyl bromide, and according to the process described in the Production Example 1, there was obtained 0.59 g of 2-(2,2-dimethyl-

propyl)-2-(4-(trifluoromethoxy)benzyl)malononitrile (compound 85).

Yield: 63%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.20(9H, s), 1.94(2H, s), 3.21(2H, s), 7.26(2H, d), 7.44(2H, d).

Production Example 84

Using 1.36 g of (2,2-dimethylpropyl)malononitrile, 20 ml of N,N-dimethylformamide, 0.43 g of sodium hydride (60% in oil), and 3.00 g of 4-bromobenzyl bromide, and according to the process described in the Production Example 1, there was obtained 2.74 g of 2-(4-bromobenzyl)-2-(2,2-dimethylpropyl)malononitrile (compound 86).

Yield: 90%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.19(9H, s), 1.91(2H, s), 3.16(2H, s), 7.28(2H, d), 7.54(2H, d).

Production Example 85

Using 0.50 g of (4-(trifluoromethoxy)benzyl)malononitrile, 8 ml of N,N-dimethylformamide, 96 mg of sodium hydride (60% in oil), and 0.57 g of isobytyl bromide, and according to the process described in the Production Example 1, there was obtained 0.31 g of 2-isobutyl-2-(4-(trifluoromethoxy)-benzyl)malononitrile (compound 87).

Yield: 51%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.13(6H, d), 1.88(2H, d), 2.13(1H, hept), 3.20(2H, s), 7.26(2H, d), 7.43(2H, d).

Production Example 86

Using 0.50 g of (4-(trifluoromethoxy)benzyl)malononitrile, 8 ml of N,N-dimethylformamide, 96 mg of sodium hydride (60% in oil), and 0.63 g of pentyl bromide, and according to the process described in the Production Example 1, there was obtained 0.45 g of 2-pentyl-2-(4-(trifluoromethoxy)-benzyl)malononitrile (compound 88).

Yield: 70%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 0.93(3H, t), 1.29-1.49(4H, m), 1.62-1.80(2H, m), 1.92-1.99(2H, m), 3.20(2H, s), 7.26(2H, d), 7.41(2H, d).

Production Example 87

Using 0.50 g of (3-(trifluoromethoxy)benzyl)malononitrile, 20 ml of N,N-dimethylformamide, 92 mg of sodium hydride (60% in oil), and 0.38 g of allyl bromide, and according to the process described in the Production Example 1, there was obtained 0.54 g of 2-allyl-2-(3-(trifluoromethoxy)-benzyl)malononitrile (compound 89).

Yield: 93%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.70-2.75(2H, m), 3.21(2H, s), 5.30-5.51(2H, m), 5.86-6.02(1H, m), 7.25-7.50(4H, m).

Production Example 88

Using 0.50 g of (3-(trifluoromethoxy)benzyl)malononitrile, 20 ml of N,N-dimethylformamide, 92 mg of sodium hydride (60% in oil), and 420 mg of 4-bromo-1-butene, and according to the process described in the Production Example 1, there was obtained 0.28 g of 2-(3-butenyl)-2-(3-(trifluoromethoxy)benzyl)malononitrile (compound 90).

Yield: 46%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.00-2.09(2H, m), 2.41-2.53(2H, m), 3.24(2H, s), 5.07-5.21(2H, m), 5.73-5.89(1H, m), 7.25-7.50(4H, m).

Production Example 89

First, 1.0 g of (4-methoxybenzylidene)malononitrile was dissolved in 30 ml of tetrahydrofuran, to which 0.57 g of trimethylsilyl cyanide was added at room temperature under a atmosphere of nitrogen, followed by stirred for 30 minutes. Then, 5.5 ml of tetrabutylammonium fluoride (1.0 M solution of tetrahydrofuran) was added dropwise to the mixture under ice-cooling, followed by stirred for 4 hours keeping ice-cooling. Then, 0.98 g of allyl

bromide was added dropwise followed by stirring overnight at room temperature. Then, a saturated ammonium chloride aqueous solution was added to the reaction mixture, which was extracted diethyl ether. The organic layer was successively washed with water, a saturated sodium chloride aqueous solution, dried over anhydrous magnesium sulfate, and then concentrated under reduced pressure. The residue was subjected to silica gel column chromatography to give 1.0 g of 2-allyl-2-(4-methoxy-α-cyanobenzyl)malononitrile (compound 91).

Yield: 76%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.98(2H, ddd), 3.85(3H, s), 4.26(1H, s), 5.54-5.62(2H, m), 5.87-6.07(1H, m), 7.04(2H, d), 7.47(2H, d).

Production Example 90

Using 1.0 g of (4-methylbenzyliden)malononitrile, 30 ml of tetrahydrofuran, 0.62 g of trimethylsilyl cyanide, 6.0 ml of tetrabutylammonium fluoride (1.0 M solution of tetrahydrofuran), and 1.08 g of allyl bromide, and according to the process described in the Production Example 89, there was obtained 1.0 g of 2-allyl-2-(4-methyl-α-cyanobenzyl)malononitrile (compound 92).

Yield: 76%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.41(3H, s), 2.96(2H, ddd), 4.23(1H, s), 5.54-5.60(2H, m), 5.87-6.01(1H, m), 7.31(2H, d), 7.43(2H, d).

Production Example 91

Using 0.50 g of (4-(methoxycarbonyl)benzylidene)malononitrile, 70 mg of tris(dibenzylideneacetone)dipalladium-chloroform complex, 0.14 g of 1,1'-bis(diphenylphosphino)ferrocene, 12 ml of tetrahydrofuran, and 0.37 g of allyl chloride, and according to the process described in the Production Example 53, there was obtained 0.31 g of 2-allyl-2-(4-(methoxycarbonyl)-α-cyanobenzyl)malononitrile (compound 93).

Yield: 48%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.92-3.13(2H, m), 3.96(3H, s), 4.32(1H, s), 5.57-5.65(2H, m), 5.89-6.03(1H, m), 7.65(2H, d), 8.19(2H, d).

Production Example 92

Using 0.3 g of (3-butenyl)malononitrile, 5 ml of N,N-dimethylformamide, 0.1 g of sodium hydride (60% in oil), and 0.72 g of 3,5-bis(trifluoromethyl)benzyl bromide, and according to the process described in the Production Example 1, there was obtained 0.12 g of 2-(3,5-bis(trifluoromethyl)-benzyl)-2-(3-butenyl)malononitrile (compound 94).

Yield: 14%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.08-2.13(2H, m), 2.48-2.56(2H, m), 3.34(2H, s), 5.14-5.23(2H, m), 5.78-5.87(1H, m), 7.86(2H, s), 7.95(1H, s).

Production Example 93

First, 0.72 g of 2,3-dimethoxybenzyl bromide was dissolved in 3 ml of N,N-dimethylformamide, to which a suspension 0.05 g of sodium hydride (60% in oil) and 0.3 g of allylmalononitrile in 2ml of N,N-dimethylformamide was added dropwise, while stirring under ice cooling, followed by further stirring at 0°C for 4 hours. Then, 10% hydrochloric acid was added to the reaction mixture, which was extracted with ethyl acetate. The organic layer was successively washed with water, a saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, and then concentrated under reduced pressure. The residue was subjected to silica gel column chromatography to give 0.34 g of 2-allyl-2-(2,3-dimethoxybenzyl)-malononitrile (compound 95).

Yield: 46%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.67(2H, d), 3.31(2H, s), 3.88(3H, s), 3.90(3H, s), 5.37-5.94(2H, m), 5.84-6.01(1H, s), 6.90-7.06(3H, m).

Production Example 94

Using 0.47 g of 4-vinylbenzyl chloride, 5 ml of N,N-dimethylformamide, 0.13 g of sodium hydride (60% in oil), and 0.3 g of allylmalononitrile, and according to the process described in the Production Example 93, there was obtained 0.22 g of 2-allyl-2-(4-vinylbenzyl)malononitrile (compound 96).

Yield: 35%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.69(2H, d), 3.19(2H, s), 5.29(1H, dd), 5.44(2H, dd), 5.77(1H, dd), 5.89-6.04(1H, m), 6.72(1H, dd), 7.33(2H, d), 7.44(2H, d).

Production Example 95

Using 0.40 g of 4-acetylbenzyl chloride, 5 ml of N,N-dimethylformamide, 0.08 g of sodium hydride (60% in oil), and 0.2 g of allylmalononitrile, and according to the process described in the Production Example 93, there was obtained 0.25 g of 2-(4-acetylbenzyl)-2-allylmalononitrile (compound 97).

Yield: 56%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.63(3H, s), 2.73(2H, d), 3.22(2H, s), 4.89-5.02(2H, m), 5.87-6.05(1H, m), 7.49(2H, d), 7.97(2H, d).

Production Example 96

Using 0.30 g of 2-(3-butenyl)-2-(4-hydroxybenzyl)malononitrile, 5 ml of N,N-dimethylformamide, 60 mg of sodium hydride (60% in oil), and 0.18 g of ethyl bromide, and according to the process described in the Production Example 78, there was obtained 255 mg of 2-(3-butenyl)-2-(4-ethoxybenzyl)-malononitrile (compound 98).

Yield: 75%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.42(3H, t), 1.96-2.04(2H, m), 2.39-2.55(2H, m), 3.17(2H, s), 4.04(2H, q), 5.08-5.19(2H, m), 5.71-5.92(1H, m), 6.90(2H, bd), 7.27(2H, bd).

Production Example 97

Using 0.30 g of 2-(3-butenyl)-2-(4-hydroxybenzyl)malononitrile, 5 ml

of N,N-dimethylformamide, 60 mg of sodium hydride (60% in oil), and 0.28 g of propyl iodide, and according to the process described in the Production Example 78, there was obtained 215 mg of 2-(3-butenyl)-2-(4-propoxybenzyl)malononitrile (compound 99).

Yield: 60%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.04(3H, t), 1.72-1.87(2H, m), 1.97-2.04(2H, m), 2.41-2.50(2H, m), 3.17(2H, s), 3.92(2H, t), 5.08-5.20(2H, m), 5.70-5.90(1H, m), 6.90(2H, bd), 7.27(2H, bd).

Production Example 98

Using 0.30 g of 2-(3-butenyl)-2-(4-hydoroxybenzyl)malononitrile, 5 ml of N,N-dimethylformamide, 60 mg of sodium hydride (60% in oil), and 0.21 g of isopropyl bromide, and according to the process described in the Production Example 78, there was obtained 227 mg of 2-(3-butenyl)-2-(4-isopropoxybenzyl)malononitrile (compound 100).

Yield: 64%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.34(6H, d), 1.97-2.04(2H, m), 2.41-2.52(2H, m), 3.16(2H, s), 4.55(1H, hept), 5.08-5.19(2H, m), 5.72-5.89(1H, m), 6.89(2H, d), 7.26(2H, d).

Production Example 99

Using 0.72 g of 4-ethylbenzyl chloride, 5 ml of N,N-dimethylformamide, 0.19 g of sodium hydride (60% in oil), and 0.5 g of allylmalononitrile, and according to the process described in the Production Example 93, there was obtained 0.48 g of 2-allyl-2-(4-ethylbenzyl)malononitrile (compound 101).

Yield: 57%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.25(3H, t), 2.61-2.74(4H, m), 3.18(2H, s), 5.37-5.49(2H, m), 5.88-6.03(1H, m), 7.21-7.33(4H, m).

Production Example 100

Using 0.79 g of 4-isopropylbenzyl chloride, 5 ml of N,N-dimethylformamide, 0.19 g of sodium hydride (60% in oil), and 0.5 g of allylmalononitrile, and according to the process described in the Production Example 93, there was obtained 0.57 g of 2-allyl-2-(4-isopropylbenzyl)malononitrile (compound 102).

Yield: 62%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.24(6H, d), 2.68(2H, d), 2.91(1H, hept), 3.16(2H, s), 5.38-5.47(2H, m), 5.86-6.00(1H, m), 7.24(2H, d), 7.29(2H, d).

Production Example 101

Using 0.72 g of (4-(trifluoromethoxy)benzyliden)malononitrile, 20 ml of benzene, 1.99 g of allyl tributyl tin, 0.20 g of azobis(isobutyronitrile) and 2.76 g of 1,1-dimethylethyl iodide, and according to the process described in the Production Example 30, there was obtained 0.20 g of 2-allyl-2-(1-(4-(trifluoromethoxy)phenyl)-2,2-dimethylpropyl)malononitrile (compound 103).

Yield: 61%;

$n_D^{20.5}$: 1.4762.

Production Example 102

Using 0.23 g of (4-(trifluoromethyl)benzyl)malononitrile, 5 ml of N,N-dimethylformamide, 0.1 g of sodium hydride (60% in oil), and 0.15 g of 1-bromopentane, and according to the process described in the Production Example 1, there was obtained 0.12 g of 2-pentyl-2-(4-(trifluoromethyl)benzyl)malononitrile (compound 104).

Yield: 46%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 0.93(3H, t), 1.34-1.45(4H, m), 1.67-1.79(2H, m), 1.94-2.00(2H, m), 3.25(2H, s), 7.51(2H, d), 7.68(2H, d).

Production Example 103

Using 0.23 g of (4-(trifluoromethyl)benzyl)malononitrile, 5 ml of

N,N-dimethylformamide, 0.1 g of sodium hydride (60% in oil), and 0.15 g of 1-bromo-3-methylbutane, and according to the process described in the Production Example 1, there was obtained 0.14 g of 2-(3-methylbutyl)-2-(4-(trifluoromethyl)benzyl)malononitrile (compound 105).

Yield: 54%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 0.96(6H, d), 1.57-1.72(3H, m), 1.96-2.04(2H, m), 3.25(2H, s), 7.52(2H, d), 7.68(2H, d).

Production Example 104

Using 0.23 g of (4-(trifluoromethyl)benzyl)malononitrile, 5 ml of N,N-dimethylformamide, 0.1 g of sodium hydride (60% in oil), and 0.15 g of 1-bromo-3-methyl-2-butene, and according to the process described in the Production Example 1, there was obtained 0.18 g of 2-(3-methyl-2-butenyl)-2-(4-(trifluoromethyl)benzyl)malononitrile (compound 106).

Yield: 68%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.73(3H, s), 1.85(3H, s), 2.74(2H, d), 3.23(2H, s), 5.34(1H, t), 7.52(2H, d), 7.68(2H, d).

Production Example 105

Using 0.23 g of (4-(trifluoromethyl)benzyl)malononitrile, 5 ml of N,N-dimethylformamide, 0.1 g of sodium hydride (60% in oil), and 0.14 g of 1-bromo-2-butene, and according to the process described in the Production Example 1, there was obtained 0.18 g of 2-(2-butenyl)-2-(4-(trifluoromethyl)-benzyl)malononitrile (compound 107).

Yield: 74%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.74(Z, 3H, dd), 1.81(E, 3H, dd), 2.68(E, 2H, d), 2.80(Z, 2H, d), 3.22(E, 2H, s), 3.25(Z, 2H, s), 5.52-5.64(1H, m), 5.81-5.95(1H, m), 7.52(2H, d), 7.68(2H, d).

Production Example 106

Using 0.23 g of (4-(trifluoromethyl)benzyl)malononitrile, 5 ml of

N,N-dimethylformamide, 0.1 g of sodium hydride (60% in oil), and 0.14 g of 3-bromo-2-methylpropen, and according to the process described in the Production Example 1, there was obtained 0.20 g of 2-(2-methyl-2-propenyl)-2-(4-(trifluoromethyl)benzyl)malononitrile (compound 108).

Yield: 71%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.99(3H, s), 2.71(2H, s), 3.27(2H, s), 5.13(1H, d), 5.21(1H, d), 7.54(2H, d), 7.69(2H, d).

Production Example 107

Using 0.23 g of (4-(trifluoromethyl)benzyl)malononitrile, 5 ml of N,N-dimethylformamide, 0.1 g of sodium hydride (60% in oil), and 0.14 g of 1-bromobutane, and according to the process described in the Production Example 1, there was obtained 0.16 g of 2-butyl-2-(4-(trifluoromethyl)benzyl)malononitrile (compound 109).

Yield: 57%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 0.98(3H, t), 1.45(2H, hex), 1.67-1.77(2H, m), 1.95-2.01(2H, m), 3.25(2H, s), 7.52(2H, d), 7.68(2H, d).

Production Example 108

Using 0.23 g of (4-(trifluoromethyl)benzyl)malononitrile, 5 ml of N,N-dimethylformamide, 0.1 g of sodium hydride (60% in oil), and 0.14 g of 1-bromo-2-methylpropane, and according to the process described in the Production Example 1, there was obtained 0.13 g of 2-(2-methylpropyl)-2-(4-(trifluoromethyl)benzyl)malononitrile (compound 110).

Yield: 46%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.13(6H, d), 1.89(2H, d), 2.07-2.20(1H, m), 3.25(2H, s), 7.52(2H, d), 7.68(2H, d).

Production Example 109

Using 0.23 g of (4-(trifluoromethyl)benzyl)malononitrile, 5 ml of N,N-dimethylformamide, 0.1 g of sodium hydride (60% in oil), and 0.15 g of

2-bromobutane, and according to the process described in the Production Example 1, there was obtained 0.07 g of 2-(1-methylpropyl)-2-(4-(trifluoromethyl)benzyl)malononitrile (compound 111).

Yield: 25%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.07(3H, t), 1.31(3H, d), 1.42-1.52(1H, m), 1.91-2.02(2H, m), 3.23(2H, dd), 7.53(2H, d), 7.68(2H, d).

Production Example 110

Using 0.23 g of (4-(trifluoromethyl)benzyl)malononitrile, 5 ml of N,N-dimethylformamide, 0.1 g of sodium hydride (60% in oil), and 0.15 g of 2-bromopentane, and according to the process described in the Production Example 1, there was obtained 0.09 g of 2-(1-methylbutyl)-2-(4-(trifluoromethyl)benzyl)malononitrile (compound 112).

Yield: 30%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.01(3H, t), 1.31(3H, d), 1.31-1.66(3H, m), 1.72-1.84(1H, m), 2.00-2.10(1H, m), 3.22(2H, dd), 7.54(2H, d), 7.68(2H, d).

Production Example 111

Using 0.23 g of (4-(trifluoromethyl)benzyl)malononitrile, 5 ml of N,N-dimethylformamide, 0.1 g of sodium hydride (60% in oil), and 0.17 g of 2-bromohexane, and according to the process described in the Production Example 1, there was obtained 0.07 g of 2-(1-methylpentyl)-2-(4-(trifluoromethyl)benzyl)malononitrile (compound 113).

Yield: 21%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 0.95(3H, t), 1.31(3H, d), 1.30-1.54(5H, m), 1.79-1.91(1H, m), 1.98-2.07(1H, m), 3.22(2H, dd), 7.53(2H, d), 7.68(2H, d).

Production Example 112

Using 0.54 g of 2,3-difluorobenzyl bromide, 5 ml of N,N-dimethyl-

formamide, 0.1 g of sodium hydride (60% in oil), and 0.28 g of allylmalononitrile, and according to the process described in the Production Example 93, there was obtained 0.31 g of 2-allyl-2-(2,3-difluorobenzyl)malononitrile (compound 114).

Yield: 52%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.74(2H, d), 3.33(2H, s), 5.41-5.49(2H, m), 5.88-5.99(1H, m), 7.15-7.26(3H, m).

Production Example 113

Using 0.69 g of (4-(2-butyloxy))benzyl bromide, 5 ml of N,N-dimethylformamide, 0.11 g of sodium hydride (60% in oil), and 0.30 g of allylmalononitrile, and according to the process described in the Production Example 93, there was obtained 0.31 g of 2-allyl-2-(4-(2-butyloxy)benzyl)-malononitrile (compound 115).

Yield: 40%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 0.97(3H, t), 1.30(3H, d), 1.56-1.78(2H, m), 2.70(2H, d), 3.16(2H, s), 4.27-4.35(1H, m), 5.39-5.47(2H, m), 5.84-6.01(1H, m), 6.91(2H, d), 7,27(2H, d).

Production Example 114

Using 0.80 g of 4-fluoro-3-phenoxybenzyl bromide, 5 ml of N,N-dimethylformamide, 0.11 g of sodium hydride (60% in oil), and 0.30 g of allylmalononitrile, and according to the process described in the Production Example 93, there was obtained 0.32 g of 2-allyl-2-(4-fluoro-3-phenoxybenzyl)malononitrile (compound 116).

Yield: 37%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.69(2H, d), 3.10(2H, s), 5.37-5.47(2H, m), 5.86-5.97(1H, m), 7.01-7.37(8H, m).

Production Example 115

Using 0.70 g of 4-(*p*-tolylthio)benzyl chloride, 5 ml of N,N-dimethyl-

formamide, 0.11 g of sodium hydride (60% in oil), and 0.30 g of allylmalononitrile, and according to the process described in the Production Example 93, there was obtained 0.38 g of 2-allyl-2-(4-(*p*-tolylthio)benzyl)malononitrile (compound 117).

Yield: 37%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.34(3H, s), 2.69(2H, d), 3.15(2H, s), 5.39-5.48(2H, m), 5.86-5.98(1H, m), 7.23-7.25(8H, m).

Production Example 116

Using 0.74 g of 3-phenoxybenzyl bromide, 5 ml of N,N-dimethylformamide, 0.11 g of sodium hydride (60% in oil), and 0.30 g of allylmalononitrile, and according to the process described in the Production Example 93, there was obtained 0.54 g of 2-allyl-2-(3-phenoxybenzyl)malononitrile (compound 118).

Yield: 67%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.70(2H, d), 3.15(2H, s), 5.37-5.47(2H, m), 5.87-5.98(1H, m)6.91-7.08(6H, m), 7.28-7.37(3H, m).

Production Example 117

Using 0.66 g of 4-(*m*-tolyloxy)benzyl bromide, 5 ml of N,N-dimethylformamide, 0.11 g of sodium hydride (60% in oil), and 0.30 g of allylmalononitrile, and according to the process described in the Production Example 93, there was obtained 0.38 g of 2-allyl-2-(4-(*m*-tolyloxy)benzyl)malononitrile (compound 119).

Yield: 45%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.35(3H, s), 2.71(2H, d), 3.17(2H, s), 5.44(2H, dd), 5.86-6.04(1H, m), 6.81-7.01(4H, m), 7.20-7.35(4H, m).

Production Example 118

Using 0.30 g of (2,4,6-trifluorobenzyl)malononitrile, 5 ml of N,N-dimethylformamide, 0.06 g of sodium hydride (60% in oil), and 0.17 g of allyl

bromide, and according to the process described in the Production Example 1, there was obtained 0.21 g of 2-allyl-2-(2,4,6-trifluorobenzyl)malononitrile (compound 120).

Yield: 59%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.75(2H, d), 3.31(2H, s), 5.37-5.46(2H, m), 5.90-6.01(1H, m), 6.81(2H, dd).

Production Example 119

Using 0.84 g of 4-(4-chlorophenoxy)benzyl bromide, 5 ml of N,N-dimethylformamide, 0.11 g of sodium hydride (60% in oil), and 0.30 g of allylmalononitrile, and according to the process described in the Production Example 93, there was obtained 0.50 g of 2-allyl-2-(4-(*p*-chlorophenoxy)benzyl)malononitrile (compound 121).

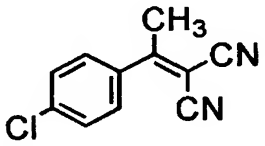
Yield: 55%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.72(2H, d), 3.17(2H, s), 5.41-5.49(2H, m), 5.88-6.00(1H, m), 6.96-7.01(4H, m), 7.25-7.36(4H, m).

The following will describe some production examples for intermediate compounds as reference production examples.

Reference Production Example 1

First, 1.00 g of (4-chloro-α-methylbenzylidene)malononitrile of the formula:



was dissolved in 20 ml of diethyl ether, to which a catalytic amount of copper (I) iodide was added, and while stirring under ice cooling, a solution of methyl magnesium iodide in diethyl ether (prepared from 0.30 g of magnesium, 10 ml of diethyl ether, and 0.86 ml of methyl iodide) was added dropwise, followed by stirring for 30 minutes under ice cooling. Then, 10%

hydrochloric acid was added to the reaction mixture, which was extracted with ethyl ether. The organic layer was successively washed with 10% hydrochloric acid, a saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, and then concentrated under reduced pressure. The residue was subjected to silica gel column chromatography to give 0.74 g of (1-(4-chlorophenyl)-1-methylethyl)malononitrile (the intermediate (2)).

Yield: 69%.

Reference Production Example 2

First, 1.02 g of (4-chlorobenzylidene)malononitrile was dissolved in 20 ml of tetrahydrofuran, to which a catalytic amount of copper (I) iodide was added, and while stirring under ice cooling, a solution of isopropyl magnesium bromide in tetrahydrofuran (prepared from 0.34 g of magnesium, 10 ml of tetrahydrofuran, and 1.46 ml of isopropyl bromide) was added dropwise, followed by stirring for 30 minutes under ice cooling. Then, 10% hydrochloric acid was added to the reaction mixture, which became acidic and was extracted with ethyl ether. The organic layer was successively washed with 10% hydrochloric acid, a saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, and then concentrated under reduced pressure. The residue was subjected to silica gel column chromatography to give 0.66 g of (1-(4-chlorophenyl)-2-methylpropyl)malononitrile (the intermediate (3)).

Yield: 52%.

Reference Production Example 3

First, 4.44 g of (4-(trifluoromethyl)benzylidene)malononitrile was dissolved in 20 ml of ethanol, and while stirring at room temperature, a suspension of 0.19 g of sodium borohydride in 5 ml of ethanol was added dropwise, followed by stirring at room temperature for 30 minutes. Then, 10%

hydrochloride acid was added to the reaction mixture, which became acidic and was extracted with diethyl ether. The organic layer was successively washed with 10% hydrochloric acid, a saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, and then concentrated under reduced pressure. The residue was subjected to silica gel column chromatography to give 2.30 g of (4-(trifluoromethyl)benzyl)malononitrile (the intermediate (4)).

Yield: 51%.

Reference Production Example 4

First, 3.00 g of (4-chloro-α-methylbenzylidene)malononitrile was dissolved in 20 ml of ethanol, and while stirring at room temperature, a suspension of 0.15 g of sodium borohydride in 5 ml of ethanol was added dropwise, followed by stirring at room temperature for 30 minutes. Then, 10% hydrochloride acid was added to the reaction mixture, which was extracted with diethyl ether. The organic layer was successively washed with 10% hydrochloric acid, a saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, and then concentrated under reduced pressure. The residue was subjected to silica gel column chromatography to give 1.70 g of (1-(4-chlorophenyl)ethyl)malononitrile (the intermediate (6)).

Yield: 56%.

Reference Production Example 5

First, 10.0 g of 4-(trifluoromethoxy)benzaldehyde and 3.50 g of malononitrile were dissolved in 60 ml of 70% (w/w) aqueous ethanol, to which a catalytic amount of benzyltrimethylammonium hydroxide was added, and the mixture was stirred at room temperature overnight. Then, a saturated aqueous sodium chloride solution was added to the reaction mixture, which was extracted with ethyl acetate. The organic layer was washed with a saturated aqueous sodium chloride solution, dried over anhydrous magne-

sium sulfate, and then concentrated under reduced pressure. The residue was recrystallized from t-butyl methyl ether and hexane to give 9.24 g of (4-(trifluoromethoxy)benzylidene)malononitrile.

Yield: 74%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 7.37 (2H, d), 7.76 (1H, s), 7.98 (2H, d).

Then, 2.61 g of (4-(trifluoromethoxy)benzylidene)malononitrile was dissolved in 20 ml of tetrahydrofuran, and while stirring at room temperature, a suspension of 0.11 g of sodium borohydride in 5 ml of ethanol was added dropwise, followed by stirring at room temperature for 30 minutes. Then, 10% hydrochloric acid was added, and the mixture was extracted with diethyl ether. The organic layer was successively washed with 10% hydrochloric acid, a saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, and then concentrated under reduced pressure. The residue was subjected to silica gel column chromatography to give 2.20 g of (4-(trifluoromethoxy)benzyl)malononitrile (the intermediate (7)).

Yield: 83%.

Reference Production Example 6

Using 1.19 g of (4-(trifluoromethoxy)benzylidene)malononitrile, 20 ml of tetrahydrofuran, a catalytic amount of copper (I) iodide, and a solution of isopropyl magnesium bromide in tetrahydrofuran (prepared from 0.39 g of magnesium, 10 ml of tetrahydrofuran, and 2.36 g of isopropyl bromide), and according to the process described in Reference Production Example 2, there was obtained 0.77 g of (1-(4-(trifluoromethoxy)phenyl)-2-methylpropyl)malononitrile (the intermediate (8)).

Yield: 55%.

Reference Production Example 7

Using 1.19 g of (4-(trifluoromethoxy)benzylidene)malononitrile, 20 ml of

tetrahydrofuran, a catalytic amount of copper (I) iodide, and 12.5 ml of a solution of methyl magnesium bromide in tetrahydrofuran (about 1 M, available from Tokyo Kasei Kogyo Co., Ltd), and according to the process described in Reference Production Example 2, there was obtained 0.76 g of (1-(4-(trifluoromethoxy)phenyl)ethyl)malononitrile (the intermediate (10)).

Yield: 60%.

Reference Production Example 8

First, 4.46 g of (3,4-dichlorobenzylidene)malononitrile was dissolved in 20 ml of tetrahydrofuran, and while stirring at room temperature, a suspension of 0.19 g of sodium borohydride in 5 ml of ethanol was added dropwise, followed by stirring at room temperature for 30 minutes. Then, 10% hydrochloride acid was added and the mixture was extracted with diethyl ether. The organic layer was successively washed with 10% hydrochloric acid, a saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, and then concentrated under reduced pressure. The residue was subjected to silica gel column chromatography to give 3.15 g of (3,4-dichlorobenzyl)malononitrile (the intermediate (12)).

Yield: 70%.

Reference Production Example 9

Using 4.46 g of (2,4-dichlorobenzylidene)malononitrile, 20 ml of tetrahydrofuran, and a suspension of 0.19 g of sodium borohydride in 5 ml of ethanol, and according to the process described in Reference Production Example 8, there was obtained 3.10 g of (2,4-dichlorobenzyl)malononitrile (the intermediate (13)).

Yield: 69%.

Reference Production Example 10

First, 10.0 g of 4-(trifluoromethylthio)benzaldehyde and 2.92 g of malononitrile were dissolved in 50 ml of 70% (w/w) aqueous ethanol, to

which a catalytic amount of benzyltrimethylammonium hydroxide was added, and the mixture was stirred at room temperature overnight. Then, a saturated aqueous sodium chloride solution was added to the reaction mixture, which was extracted with ethyl acetate. The organic layer was washed with a saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, and then concentrated under reduced pressure. The residue was recrystallized with a solvent system consisting of t-butyl methyl ether and hexane to give 10.5 g of (4-(trifluoromethylthio)benzylidene)malononitrile.

Yield: 85%;

^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 7.78 (1H, s), 7.79 (2H, d), 7.93 (2H, d).

Then, 8.00 g of (4-(trifluoromethylthio)benzylidene)malononitrile and 3.35 g of benzaldehyde were dissolved in 320 ml of ethanol, and while stirring at room temperature, 3.41g of phenylenediamine was slowly added, and the mixture was stirred at room temperature for 5 hours. Then, the reaction mixture was concentrated, 300 ml of t-butyl methyl ether was added, and insoluble matters were filtered. The filtrate was concentrated and the resulting residue was subjected to silica gel chromatography to give 6.22 g of (4-(trifluoromethylthio)benzyl)malononitrile (the intermediate (14)).

Yield: 77%.

Reference Production Example 11

First, 9.78 g of malononitrile, 954 mg of tetrabutylammonium bromide, and 10.0 g of 4-bromo-1-butene were mixed, and while stirring at 0°C under an atmosphere of nitrogen, 8.3 g of potassium t-butoxide was slowly added. The mixture was further stirred at room temperature for 12 hours. Then, the reaction mixture was poured into water, followed by extraction with t-butyl methyl ether. The organic layer was washed with

water, a saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, and then concentrated under reduced pressure. The residue was subjected to silica gel column chromatography to give 2.31 g of (3-butenyl)malononitrile (the intermediate (16)).

Yield: 26%.

Reference Production Example 12

Using 4.00 g of (4-(trifluoromethoxy)benzylidene)malononitrile, 30 ml of tetrahydrofuran, 175 mg of copper (I) bromide dimethyl sulfide complex, and 26 ml of a solution (0.98 M) of vinyl magnesium bromide in tetrahydrofuran, and according to the process described in Reference Production Example 2, there was obtained 1.60 g of (1-(4-trifluoromethoxyphenyl))-2-propenylmalononitrile (the intermediate (18)).

Reference Production Example 13

Using 5.00 g of (2-methoxybenzylidene)malononitrile, 40 ml of tetrahydrofuran, and a suspension of 0.31 g of sodium borohydride in 10 ml of ethanol, and according to the process described in Reference Production Example 8, there was obtained 3.56 g of (2-methoxybenzyl)malononitrile (the intermediate (20)).

Yield: 70%.

Reference Production Example 14

First, 9.18 g of (4-hydroxybenzyl)malononitrile was dissolved in 90 ml of N,N-dimethylformamide, to which 2.56 g of sodium hydride (60% in oil) was added, while stirring under ice cooling. After the evolution of hydrogen gas ceased, while stirring under ice cooling, 7.21 g of 4-bromo-1-betene was added dropwise, followed by further stirring at room temperature overnight. Then, a saturated aqueous ammonium chloride solution was added to the reaction mixture, which was extracted with diethyl ether. The organic layer was successively washed with water, a saturated aqueous sodium chloride

solution, dried over anhydrous magnesium sulfate, and then concentrated under reduced pressure. The residue was subjected to silica gel column chromatography to give 10.3 g of 2-(3-butenyl)-2-(4-hydroxybenzyl)malononitrile (the intermediate (23)).

Yield: 86%.

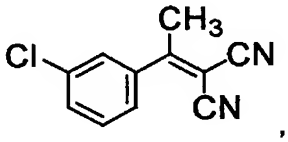
Reference Production Example 15

Using 5.23 g of (4-ethoxybenzylidene)malononitrile, 40 ml of tetrahydrofuran, and a suspension of 0.35 g of sodium borohydride in 10 ml of ethanol, and according to the process described in Reference Production Example 8, there was obtained 2.76 g of (4-ethoxybenzyl)malononitrile (the intermediate (25)).

Yield: 52%.

Reference Production Example 16

Using 3.00 g of (3-chloro-α-methylbenzylidene)malononitrile of the formula:

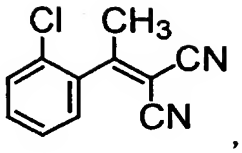


60 ml of diethyl ether, a catalytic amount of copper (I) iodide, and methyl magnesium iodide in diethyl ether (prepared from 0.90 g of magnesium, 30 ml of diethyl ether, and 2.58 ml of methyl iodide), and according to the process described in Reference Production Example 1, there was obtained 2.33g of (1-(3-chlorophenyl)-1-methylethyl)malononitrile (the intermediate (26)).

Yield: 73%.

Reference Production Example 17

Using 3.00 g of (2-chloro-α-methylbenzylidene)malononitrile of the formula:



60 ml of diethyl ether, a catalytic amount of copper (I) iodide, and methyl magnesium iodide in diethyl ether (prepared from 0.90 g of magnesium, 30 ml of diethyl ether, and 2.58 ml of methyl iodide), and according to the process described in Reference Production Example 1, there was obtained 1.16g of (1-(2-chlorophenyl)-1-methylethyl)malononitrile (the intermediate (27)).

Yield: 36%.

Reference Production Example 18

Using 4.46 g of (2,3-dichlorobenzylidene)malononitrile, 20 ml of tetrahydrofuran, and a suspension of 0.21 g of sodium borohydride in 5 ml of ethanol, and according to the process described in Reference Production Example 8, there was obtained 3.07 g of (2,3-dichlorobenzyl)malononitrile (the intermediate (29)).

Yield: 68%.

Reference Production Example 19

Using 4.46 g of (2,6-dichlorobenzylidene)malononitrile, 20 ml of tetrahydrofuran, and a suspension of 0.21 g of sodium borohydride in 5 ml of ethanol, and according to the process described in Reference Production Example 8, there was obtained 2.73 g of (2,6-dichlorobenzyl)malononitrile (the intermediate (30)).

Yield: 61%.

Reference Production Example 20

Using 4.88 g of (2,3,4,5,6-pentafluorobenzylidene)malononitrile, 20 ml of tetrahydrofuran, and a suspension of 0.21 g of sodium borohydride in 5 ml of ethanol, and according to the process described in Reference Production

Example 8, there was obtained 2.20 g of (2,3,4,5,6-pentafluorobenzyl)-malononitrile (the intermediate (31)).

Yield: 45%.

Reference Production Example 21

Using 1.02 g of (3-chlorobenzylidene)malononitrile, 20 ml of tetrahydrofuran, a catalytic amount of copper (I) iodide, and 10ml of isopropyl magnesium bromide in tetrahydrofuran (1.4 M), and according to the process described in Reference Production Example 2, there was obtained 0.71 g of (1-(3-chlorophenyl)-2-methylpropyl)malononitrile (the intermediate (32)).

Yield: 56%.

Reference Production Example 22

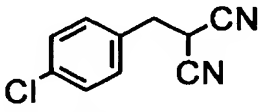
First, 13.2 g of (2,2-dimethylpropylidene)malononitrile and 10.5 g of benzaldehyde was dissolved in 800 ml of ethanol, to which 10.6 g of 1,2-phenylenediamine was added slowly while stirring, followed by stirring overnight at room temperature. Then, the reaction mixture was concentrated under reduced pressure. Then, 300 ml of chloroform was added to the residue, the precipitate was filtered off, the filtrate was concentrated. And the same operation was repeated once more. The residue was subjected to silica gel column chromatography to give 8.50 g of (2,2-dimethylpropyl)malononitrile (the intermediate (34)).

Yield: 64%.

The intermediate compounds used in the production of the compounds are shown below with the compound numbers and physical data.

Intermediate (1)

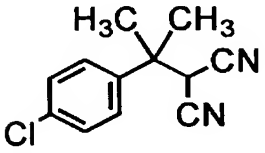
(4-Chlorobenzyl)malononitrile



m.p.: 96.9°C.

Intermediate (2)

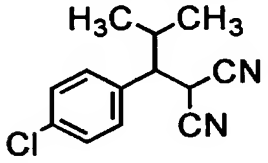
(1-(4-Chlorophenyl)-1-methylethyl)malononitrile



$n_D^{22.0}$: 1.5372.

Intermediate (3)

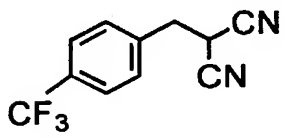
(1-(4-Chlorophenyl)-2-methylpropyl)malononitrile



$n_D^{21.5}$: 1.5289.

Intermediate (4)

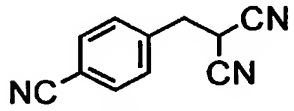
(4-(Trifluoromethyl)benzyl)malononitrile



m.p.: 79.1°C.

Intermediate (5)

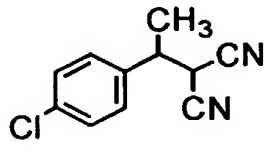
(4-Cyanobenzyl)malononitrile



m.p.: 118.7°C.

Intermediate (6)

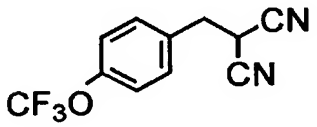
(1-(4-Chlorophenyl)ethyl)malononitrile



$n_D^{24.5}$: 1.5349.

Intermediate (7)

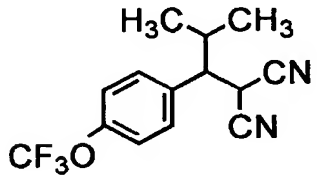
(4-(Trifluoromethoxy)benzyl)malononitrile



m.p.: 88.3°C.

Intermediate (8)

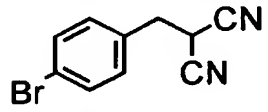
(1-(4-(Trifluoromethoxy)phenyl-2-methylpropyl)malononitrile



^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 0.83 (3H, d), 1.16 (3H, d), 2.29-2.45 (1H, m), 2.87 (1H, dd), 4.18 (1H, d), 7.25-7.30 (2H, m), 7.38-7.42 (2H, m).

Intermediate (9)

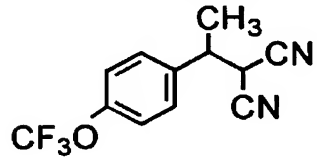
(4-Bromobenzyl)malononitrile



m.p.: 97.7°C.

Intermediate (10)

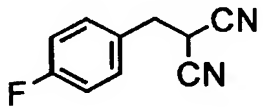
(1-(4-(Trifluoromethoxy)phenyl)ethyl)malononitrile



^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.65 (3H, d), 3.49 (1H, dq), 3.85 (1H, d), 7.24-7.29 (2H, m), 7.38-7.42 (2H, m).

Intermediate (11)

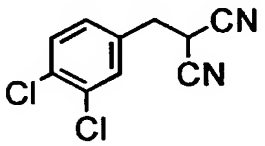
(4-Fluorobenzyl)malononitrile



m.p.: 117.2°C.

Intermediate (12)

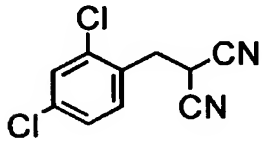
(3,4-Dichlorobenzyl)malononitrile



m.p.: 83.3°C.

Intermediate (13)

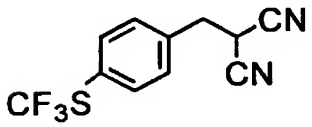
(2,4-Dichlorobenzyl)malononitrile



m.p.: 62.5°C.

Intermediate (14)

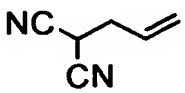
(4-(Trifluoromethylthio)benzyl)malononitrile



^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 3.15 (2H, d), 3.95 (1H, t), 7.37 (2H, d), 7.70 (2H, d).

Intermediate (15)

Allylmalononitrile

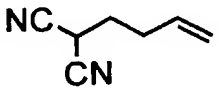


^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.75 (2H, dd), 3.79 (1H, t), 5.36-5.45

(2H, m), 5.75-5.94 (1H, m).

Intermediate (16)

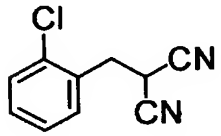
(3-Butenyl)malononitrile



^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 2.11-2.18 (2H, m), 2.31-2.41 (2H, m), 3.76 (1H, t), 5.16-5.26 (2H, m), 5.64-5.79 (1H, m).

Intermediate (17)

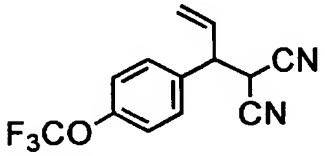
(2-chlorobenzyl)malononitrile



$n_D^{19.5}$: 1.5384.

Intermediate (18)

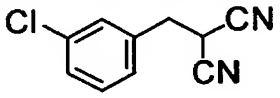
(1-(4-Trifluoromethoxyphenyl)-2-propenyl)malononitrile



^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 3.95-4.03 (2H, m), 5.40-5.53 (2H, m), 6.08-6.19 (1H, m), 7.28 (2H, d), 7.39 (2H, d).

Intermediate (19)

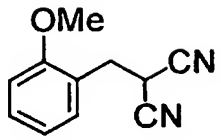
(3-chlorobenzyl)malononitrile



$n_D^{19.5}$: 1.5403.

Intermediate (20)

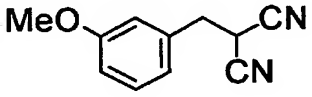
(2-methoxybenzyl)malononitrile



$n_D^{19.5}$: 1.5248.

Intermediate (21)

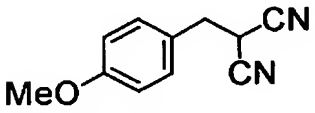
(3-methoxybenzyl)malononitrile



m.p.: 55.5°C.

Intermediate (22)

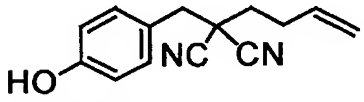
(4-methoxybenzyl)malononitrile



m.p.: 89.6°C.

Intermediate (23)

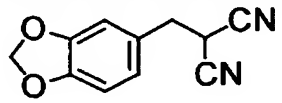
2-(3-butenyl)-2-(4-hydroxybenzyl)malononitrile



^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.99-2.05(2H, m), 2.43-2.51(2H, m), 3.16(2H, s), 4.99(1H, bs), 5.09-5.20(2H, m), 5.74-5.86(1H, m), 6.85(2H, d), 7.24(2H, d).

Intermediate (24)

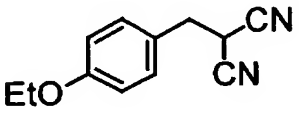
(3,4-(methylenedioxy)benzyl)malononitrile



^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 3.19(2H, d), 3.87(1H, t), 5.98(2H, s), 6.73-6.83(3H, m).

Intermediate (25)

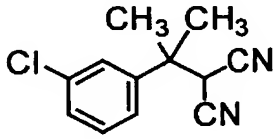
(4-ethoxybenzyl)malononitrile



m.p.: 118.0°C.

Intermediate (26)

(1-(3-chlorophenyl)-1-methylethyl)malononitrile



$n_D^{23.0}$: 1.5376.

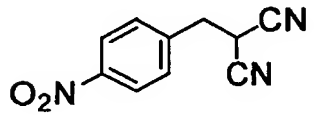
Intermediate (27)

(1-(2-chlorophenyl)-1-methylethyl)malononitrile

m.p.: 90.2°C.

Intermediate (28)

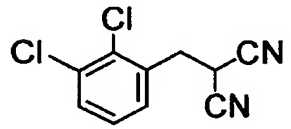
(4-nitrobenzyl)malononitrile



m.p.: 155.7°C.

Intermediate (29)

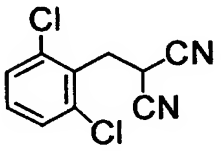
(2,3-dichlorobenzyl)malononitrile



$n_D^{22.5}$: 1.5518.

Intermediate (30)

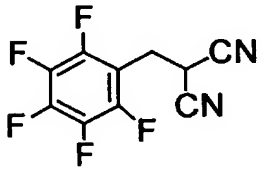
(2,6-dichlorobenzyl)malononitrile



m.p.: 87.7°C.

Intermediate (31)

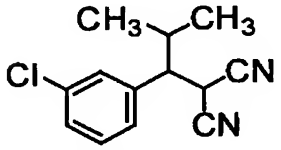
(2,3,4,5,6-pentafluorobenzyl)malononitrile



m.p.: 96.3°C.

Intermediate (32)

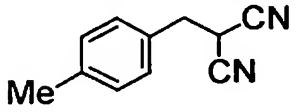
(1-(3-chlorophenyl)-2-methylprpyl)malononitrile



$n_D^{21.5}$: 1.5268.

Intermediate (33)

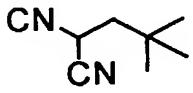
(4-methylbenzyl)malononitrile



m.p.: 83.7°C.

Intermediate (34)

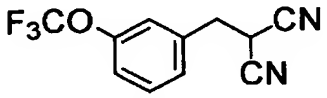
(2,2-dimethylpropyl)malononitrile



^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 1.07(9H, s), 2.04(2H, d), 3.66(1H, t).

Intermediate (35)

(3-(trifluoromethoxy)benzyl)malononitrile

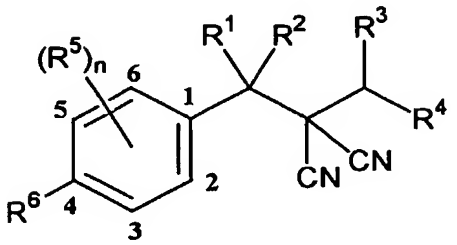


^{1}H-NMR ($CDCl_3$, TMS, δ (ppm)): 3.34(2H, d), 3.97(1H, t), 7.25-7.50(4H, m).

Specific examples of the compounds (X) are shown in Table 1 with their compound numbers.

TABLE 1

The compounds of formula (X):



(X)

No.	R^1	R^2	R^3	R^4	$(R^5)_m$	R^6
1	H	H	H	$CH=CH_2$	–	Cl
2	CH_3	CH_3	H	$CH=CH_2$	–	Cl
3	H	$CH(CH_3)_2$	H	$CH=CH_2$	–	Cl
4	H	H	H	$CH_2CH=CH_2$	–	Cl
5	H	H	H	$CH=CH_2$	–	CF_3
6	H	H	H	$CH_2CH=CH_2$	–	CN
7	H	H	H	$(CH_2)_2CH=CH_2$	–	CN
8	H	H	H	$CH=CH_2$	2-Cl	H
9	H	H	$CH_2CH_2CH_2CH_2CH_2$		–	Cl
10	H	CH_3	H	$CH_2CH=CH_2$	–	Cl
11	H	H	H	$CH=CH_2$	–	OCF_3
12	H	$CH(CH_3)_2$	H	$CH_2CH=CH_2$	–	OCF_3
13	H	H	H	$CH=CH_2$	–	Br
14	H	H	H	$CH=CH_2$	–	CN
15	H	H	H	$CH_2CH=CH_2$	–	OCF_3
16	H	CH_3	H	$CH_2CH=CH_2$	–	OCF_3
17	H	H	H	$CH=CH_2$	3-Cl	H
18	H	H	H	$CH=CH_2$	–	F
19	H	H	H	$CH(CH_3)_2$	–	Cl

TABLE 1 (contn'd)

No.	R^1	R^2	R^3	R^4	$(R^5)_m$	R^6
20	H	H	H	$CH=CH_2$	2-OCH_3	H
21	H	H	H	$(CH_2)_2CH=CH_2$	–	Cl
22	H	H	CH_3	$CH=CH_2$	–	Cl
23	H	H	H	$CH=CH_2$	3-Cl	Cl
24	H	H	H	$CH=CH_2$	2-Cl	Cl
25	H	H	H	$CH=C(CH_3)_2$	–	Cl
26	H	$CH(CH_3)_2$	H	$CH_2CH=CH_2$	–	Cl
27	H	H	H	$CH=C(CH_3)_2$	–	OCF_3
28	H	H	H	$CH=CH_2$	3-OCH_3	H
29	H	H	H	$CH=CH_2$	–	OCH_3
30	H	CH_3	H	$CH=CH_2$	–	OCF_3
31	H	CH_2Cl	H	$CH=CH_2$	–	OCF_3
32	H	$CH=CH_2$	H	$CH_2CH=CH_2$	–	OCF_3
33	H	$CH=CH_2$	H	$CH=CH_2$	–	OCF_3
34	H	$CH=CH_2$	H	$C\equiv CH$	–	OCF_3
35	H	H	H	$CH_2CH=CH_2$	–	$OCBrF_2$
36	H	H	H	$CH_2CH=CH_2$	–	$OCHF_2$
37	H	H	H	$CH_2CH=CH_2$	3,4-OCH_2O	
38	H	H	H	$CH_2CH=CH_2$	–	$OCH_2CH=CH_2$
39	H	OCH_3	H	$CH=CH_2$	–	OCF_3
40	H	OCH_2CF_3	H	$CH=CH_2$	–	OCF_3
41	H	H	H	$CH=CH_2$	–	SCF_3
42	H	H	H	$CH_2CH=CH_2$	–	SCF_3
43	H	OCH_3	H	$CH=CH_2$	–	SCF_3
44	H	H	H	$CH=CH_2$	–	OCH_2CH_3

TABLE 1 (contn'd)

No.	R^1	R^2	R^3	R^4	$(R^5)_m$	R^6
45	H	H	H	$CH_2CH(CH_3)_2$	–	OCF_3
46	H	H	H	$CH=CHCH_3$	–	SCF_3
47	H	H	CH_3	$CH=CH_2$	–	SCF_3
48	CH_3	CH_3	H	$CH=CH_2$	3-Cl	H
49	CH_3	CH_3	H	$CH=CH_2$	2-Cl	H
50	H	H	H	$CH=CH_2$	–	NO_2
51	H	H	CH_3	CH_3	–	Cl
52	H	H	H	$CH_2CH=CH_2$	–	CF_3
53	H	H	H	$CH=CH_2$	2,3-Cl_2	–
54	H	H	H	$CH=CH_2$	2,6-Cl_2	–
55	H	CN	H	$CH=CH_2$	–	OCF_3
56	H	CN	H	$CH=CH_2$	–	SCF_3
57	H	H	H	$CH=CH_2$	2-CF_3	CF_3
58	H	H	H	$CH=CH_2$	2-Cl	CF_3
59	H	H	H	$C\equiv CCH_3$	–	OCF_3
60	H	H	H	$CH_2CH=CH_2$	2-Cl	CF_3
61	H	H	H	$CH=CH_2$	–	$S(O)_2CH_3$
62	H	H	H	$CH=CH_2$	2,3,5,6-F_4	F
63	H	H	H	$CH=CH_2$	2-NO_2	CF_3
64	H	H	H	$CH=CH_2$	2,6-Cl_2	CF_3
65	H	H	H	$CH_2CH=CH_2$	2,6-Cl_2	CF_3
66	H	$CH(CH_3)_2$	H	$CH=CH_2$	3-Cl	H
67	H	H	H	$CH_2CH=CH_2$	2-NO_2	CF_3
68	H	H	H	H	–	Cl
69	H	H	H	$CH=CH_2$	3-F	CF_3

TABLE 1 (contn'd)

No.	R^1	R^2	R^3	R^4	$(R^5)_m$	R^6
70	H	H	H	$CH=CH_2$	–	SCH_3
71	H	H	H	C_2H_5	–	CF_3
72	H	H	H	CH_3	–	Cl
73	H	H	H	(Z)-$CH_2CH=CHCH_2CH_3$	–	Cl
74	H	CH_3	H	$CH=CH_2$	–	Cl
75	H	H	H	CH_3	–	CF_3
76	H	CH_3	H	$CH_2CH_2CH=CH_2$	–	Cl
77	H	H	H	$CH=CH_2$	–	CH_3
78	H	H	H	$CH_2CH=CH_2$	–	$OC(=O)CH_3$
79	H	H	H	$(CH_2)_2CH=CH_2$	–	CF_3
80	H	H	H	$CH_2CH=CH_2$	–	OCF_2CF_2H
81	H	H	H	$CH_2CH=CH_2$	–	OCH_2CF_3
82	H	OCH_2CH_3	H	$CH=CH_2$	–	OCF_3
83	H	OCH_3	H	$CH=CH_2$	–	CN
84	H	OCH_3	H	$CH=CH_2$	–	Cl
85	H	H	H	$C(CH_3)_3$	–	OCF_3
86	H	H	H	$C(CH_3)_3$	–	Br
87	H	H	H	$CH(CH_3)_2$	–	OCF_3
88	H	H	H	$CH_2CH_2CH_2CH_3$	–	OCF_3
89	H	H	H	$CH=CH_2$	3-OCF_3	H
90	H	H	H	$CH_2CH=CH_2$	3-OCF_3	H
91	H	CN	H	$CH=CH_2$	–	OCH_3
92	H	CN	H	$CH=CH_2$	–	CH_3
93	H	CN	H	$CH=CH_2$	–	$C(=O)OCH_3$
94	H	H	H	$CH_2CH=CH_2$	3,5-$(CF_3)_2$	H

TABLE 1 (contn'd)

No.	R^1	R^2	R^3	R^4	$(R^5)_m$	R^6
95	H	H	H	$CH=CH_2$	2,3-$(OCH_3)_2$	H
96	H	H	H	$CH=CH_2$	–	$CH=CH_2$
97	H	H	H	$CH=CH_2$	–	$C(=O)CH_3$
98	H	H	H	$CH_2CH=CH_2$	–	OCH_2CH_3
99	H	H	H	$CH_2CH=CH_2$	–	$OCH_2CH_2CH_3$
100	H	H	H	$CH_2CH=CH_2$	–	$OCH(CH_3)_2$
101	H	H	H	$CH=CH_2$	–	CH_2CH_3
102	H	H	H	$CH=CH_2$	–	$CH(CH_3)_2$
103	H	$C(CH_3)_3$	H	$CH=CH_2$	–	OCF_3
104	H	H	H	$CH_2CH_2CH_2CH_3$	–	CF_3
105	H	H	H	$CH_2CH(CH_3)_2$	–	CF_3
106	H	H	H	$CH=C(CH_3)_2$	–	CF_3
107	H	H	H	$CH=CHCH_3$	–	CF_3
108	H	H	H	$C(CH_3)=CH_2$	–	CF_3
109	H	H	H	$CH_2CH_2CH_3$	–	CF_3
110	H	H	H	$CH(CH_3)_2$	–	CF_3
111	H	H	CH_3	CH_2CH_3	–	CF_3
112	H	H	CH_3	$CH_2CH_2CH_3$	–	CF_3
113	H	H	CH_3	$CH_2CH_2CH_2CH_3$	–	CF_3
114	H	H	H	$CH=CH_2$	2,3-F_2	H
115	H	H	H	$CH=CH_2$	–	$OCH(CH_3)CH_2CH_3$
116	H	H	H	$CH=CH_2$	3-OPh	F
117	H	H	H	$CH=CH_2$	–	S(p-CH_3Ph)
118	H	H	H	$CH=CH_2$	3-OPh	H
119	H	H	H	$CH=CH_2$	–	O(m-CH_3Ph)

TABLE 1 (contn'd)

No.	R^1	R^2	R^3	R^4	$(R^5)_m$	R^6
120	H	H	H	$CH=CH_2$	2,6-F_2	F
121	H	H	H	$CH=CH_2$	–	O(p-ClPh)
122	H	H	H	$CH_2CH(CH_3)_2$	3-Cl	Cl
123	H	H	H	$CH_2CH(CH_3)_2$	–	Cl
124	H	H	H	$CH_2CH(CH_3)_2$	–	CN
125	H	H	H	$CH_2CH(CH_3)_2$	–	NO_2
126	H	H	H	$CH_2CH(CH_3)_2$	3-F	CF_3
127	H	H	H	$CH_2CH(CH_3)_2$	3-Cl	CN
128	H	CH_3	H	$CH_2CH(CH_3)_2$	–	CF_3
129	H	CH_3	H	$CH_2CH(CH_3)_2$	–	Cl
130	H	CH_3	H	$CH_2CH(CH_3)_2$	–	CN
131	H	$CH(CH_3)_2$	H	$CH_2CH(CH_3)_2$	–	CF_3
132	H	H	H	$CH_2CH(CH_3)_2$	3-CF_3	H
133	H	H	H	$CH_2CH(CH_3)_2$	–	CF_3
134	CH_3	CH_3	H	$CH_2CH(CH_3)_2$	–	CN
135	CH_3	CH_3	H	$CH_2CH(CH_3)_2$	3-Cl	Cl
136	H	H	H	$CH_2C(CH_3)_3$	–	CF_3
137	H	H	H	$CH_2C(CH_3)_3$	–	Cl
138	H	H	H	$CH_2C(CH_3)_3$	–	CN
139	H	H	H	$CH_2C(CH_3)_3$	–	NO_2
140	H	H	H	$CH_2C(CH_3)_3$	3-Cl	CF_3
141	H	H	H	$CH_2C(CH_3)_3$	3-F	CN
142	H	CH_3	H	$CH_2C(CH_3)_3$	–	CF_3
143	H	CH_3	H	$CH_2C(CH_3)_3$	3-F	CF_3
144	H	$CH(CH_3)_2$	H	$CH_2C(CH_3)_3$	3-F	CF_3

TABLE 1 (contn'd)

No.	R^1	R^2	R^3	R^4	$(R^5)_m$	R^6
145	H	$CH(CH_3)_2$	H	$CH_2C(CH_3)_3$	–	CF_3
146	H	H	H	$CH_2C(CH_3)_3$	3-F	Cl
147	H	H	H	$CH_2C(CH_3)_3$	3-Cl	F
148	H	H	H	$CH=CH_2$	3-Cl	CF_3
149	H	CH_3	H	$CH=CH_2$	3-F	CF_3
150	H	H	H	$CH=CH_2$	3-CF_3	H
151	H	H	H	$CH=CH_2$	3-Cl	CN
152	H	H	H	$CH_2CH=CH_2$	3-Cl	CF_3
153	H	H	H	$CH_2CH=CH_2$	3-F	CF_3
154	H	H	H	$CH_2CH=CH_2$	3-F	CN
155	H	H	H	$CH_2CH=CH_2$	3-Cl	F
156	H	CH_3	H	$CH_2CH=CH_2$	3-F	Cl
157	H	CH_3	H	$CH=C(CH_3)_2$	3-F	Cl
158	H	H	H	$CH=C(CH_3)_2$	3-Cl	CF_3
159	H	H	H	$CH=C(CH_3)_2$	3-F	CF_3
160	H	$CH(CH_3)_2$	H	$CH=C(CH_3)_2$	–	CF_3
161	H	H	H	$CH=C(CH_3)_2$	3-CF_3	H
162	H	H	H	$CH_2CH=C(CH_3)_2$	–	CF_3
163	H	H	H	$CH_2CH=C(CH_3)_2$	–	CN
164	H	H	H	$CH_2CH=C(CH_3)_2$	–	NO_2
165	H	H	H	CH_2CH_3	3-F	CF_3
166	H	H	H	CH_2CH_3	–	CN
167	H	H	H	CH_2CH_3	–	Cl
168	H	H	H	CH_2CH_3	–	NO_2
169	H	CH_3	H	CH_2CH_3	–	CF_3

TABLE 1 (contn'd)

No.	R^1	R^2	R^3	R^4	$(R^5)_m$	R^6
170	H	CH_3	H	CH_2CH_3	–	CN
171	H	H	H	$CH_2CH_2CH_3$	3-F	Cl
172	H	H	H	$CH_2CH_2CH_3$	3-Cl	F
173	H	H	H	$CH_2CH_2CH_3$	3-F	CF_3
174	H	CH_3	H	$CH_2CH_2CH_3$	3-CF_3	H
175	H	H	H	CH_2CH_3	3-CF_3	H
176	H	H	H	$CH_2CH_2CH_3$	3-CF_3	H
177	H	CH_2F	H	$CH_2CH=CH_2$	–	CF_3
178	H	H	H	$CH_2CH_2CH_3$	–	SCF_3
179	H	H	H	CH_2CH_3	–	OCF_3
180	H	CF_3	H	CH_2CH_3	3-F	CF_3

The following will describe some formulation examples wherein parts represent parts by weight. The compounds (X) are designated by their compound numbers shown in Table 1.

Formulation Example 1

Nine (9) parts of each of compounds 1 to 120 is dissolved in 37.5 parts of xylene and 37.5 parts of dimethylformamide, and 10 parts of polyoxyethylene styryl phenyl ether and 6 parts of calcium dodecylbenzenesulfonate are added thereto, followed by well stirring and mixing, to give an emulsifiable concentrate for each compound.

Formulation Example 2

To 40 parts of each of compounds 1 to 120 is added 5 parts of Sorpol® 5060 (Toho Chemical Industry Co., Ltd.), followed by well mixing, and 32 parts of Carplex® #80 (synthetic hydrated silicone oxide fine powder; Shionogi & Co., Ltd.) and 23 parts of 300 mesh diatomaceous earth are added,

which is mixed with a mixer to give a wettable powder for each compound.

Formulation Example 3

To 3 parts of each of compounds 1 to 120 are added 5 parts of synthetic hydrated silicon oxide fine powder, 5 parts of sodium dodecylbenzenesulfonate, 30 parts of bentonite, and 57 parts of clay, followed by well stirring and mixing, and an appropriate amount of water is added to this mixture, followed by further stirring, granulation with a granulator, and air drying, to give a granule for each compound.

Formulation Example 4

First, 4.5 parts of each of compounds 1 to 120, 1 part of synthetic hydrated silicon oxide fine powder, 1 part of Doriresu B (Sankyo Co., Ltd.) as a flocculant, and 7 parts of clay are well mixed with a mortar, followed by stirring and mixing with a mixer. To the resulting mixture is added 86.5 parts of cut clay, followed by well stirring and mixing, to give a dust for each compound.

Formulation Example 5

Ten parts of each of compounds 1 to 120, 35 parts of white carbon containing 50 parts of polyoxyethylene alkyl ether sulfate ammonium salt, and 55 parts of water are mixed and pulverized by the wet grinding method to give a formulation for each compound.

Formulation Example 6

First, 0.5 parts of each of compounds 1 to 120 is dissolved in 10 parts of dichloromethane, which is mixed with 89.5 parts of ISOPAR® M (isoparaffin; Exxon Chemical Co.) to give an oil formulation for each compound.

Formulation Example 7

First, 0.1 parts of compounds 1 to 120 and 49.9 parts of NEOCHIOZOL (Chuo Kasei K.K.) are put into an aerosol can, to which an aerosol

valve is attached. Then, 25 parts of dimethyl ether and 25 parts of LPG are filled in the aerosol can, followed by shaking and attachment of an actuator, to give an oil-based aerosol.

Formulation Example 8

First, 0.6 parts of each of compounds 1 to 120, 0.01 parts of BHT, 5 parts of xylene, 3.39 parts of deodorized kerosine, and 1 part of an emulsifier (Atmos 300; Atmos Chemical Co.) are mixed to become a solution. Then, this solution and 50 parts of distilled water are filled in an aerosol can, to which a valve part is attached, and 40 parts of a propellant (LPG) is filled under pressure through the valve in the aerosol can to give a water-based aerosol.

The following test example will demonstrate that the compounds (X) are useful as the active ingredients of pesticide compositions. The compounds (X) are designated by their compound numbers shown in Table 1.

Test Example 1 Pesticidal Test against *Nilaparvata lugens*

Each formulation of the compound 11, 12, 16, 27, 30, 31, 32, 33, 34, 37, 40, 41, 42, 47, 49, 52, 56, 58, 59, 60, 63, 64, 65, 67, 69, 71, 75, 79, 87, 88, 89, 90, 98, 100, 102, 105, 106, 108, 109, 110, 114, 115, 116, 117, 118 and 119 obtained according to Formulation Example 5 was diluted with water so that the active ingredient concentration came to 500 ppm to prepare a test liquid for each compound.

Fifty grams of molding Bonsoru 2 (available from Sumitomo Chemical Co., Ltd.) was put into a polyethylene cup, and 10 to 15 seeds of rice were planted in the polyethylene cup. Then rice plants were grown until the second foliage leaves developed and then cut into the same height of 5 cm. The test liquid, which had been prepared as described above, was sprayed at the rate of 20 ml/cup onto these rice plants. After the test liquid sprayed onto the rice plants were dried, the polyethylene cup with the rice plants was

placed in a large polyethylene cup and 30 first-instar larvae of *Nilaparvata lugens* (brown planthopper) were set free in the large polyethylene cup, which was then kept covered and left in a greenhouse at 25°C. On the 6th day after the release of larvae of *Nilaparvata lugens*, the number of parasitic *Nilaparvata lugens* on the rice plants was examined.

As a result, in the treatment with each of the compounds described above, the number of parasitic pests on the 6th day after the treatment was not greater than 3.

Test Example 2 Pesticidal Test against *Nilaparvata lugens*

Each formulation of the compound 11, 12, 16, 41, 45, 47, 49, 52, 54, 58, 68, 69, 71, 75, 87, 90, 105, 106, 108, 109 and 110 obtained according to Formulation Example 5 was diluted with water so that the active ingredient concentration came to 45.5 ppm to prepare a test liquid for each compound.

Fifty grams of molding Bonsoru 2 (available from Sumitomo Chemical Co., Ltd.) was put into a polyethylene cup having five holes of 5 mm, and 10 to 15 seeds of rice were planted in the polyethylene cup. Then rice plants were grown until the second foliage leaves developed and the polyethylene cup with the rice plants was placed in a large polyethylene cup containing 55 ml of the test liquid, which had been prepared as described above. The rice plants were left in a greenhouse at 25°C for 6 days and then cut into the same height of 5 cm. Thirty first-instar larvae of *Nilaparvata lugens* (brown planthoppers) were set free in the large polyethylene cup, which was then kept covered and left in a greenhouse at 25°C. On the 6th day after the release of larvae of *Nilaparvata lugens*, the number of parasitic *Nilaparvata lugens* on the rice plants was examined.

As a result, in the treatment with each of the compounds described above, the number of parasitic pests on the 6th day after the treatment was not greater than 3.

Test Example 3 Pesticidal Test against *Nilaparvata lugens*

Each formulation of the compound 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 21, 22, 23, 24, 25, 26, 27, 29, 44, 48, 49, 51, 62, 66, 73, 74, 76 and 77 obtained according to Formulation Example 1 was diluted with water so that the active ingredient concentration came to 500 ppm to prepare a test liquid for each compound.

A bundle of 3 to 4 of cotyledons (height of 3 to 5 cm) of rice was immersed in the test liquid, which had been prepared as described above, for 1 minute. After the test liquid treated the rice plants was dried, a filter paper moistened with 1 ml of water was place on a bottom of polyethylene cup and then the bundle of cotyledons of rice was placed on it. Thirty first-instar larvae of *Nilaparvata lugens* (brown planthoppers) were set free in the polyethylene cup, which was then kept covered and left in a greenhouse at 25°C. On the 6th day after the release of larvae of *Nilaparvata lugens*, the number of parasitic *Nilaparvata lugens* on the rice plants was examined.

As a result, in the treatment with each of the compounds described above, the number of parasitic pests on the 6th day after the treatment was not greater than 3.

Test Example 4 Pesticidal Test against *Diabrotica undecimpunctata*

Each formulation of the compound 1, 2, 3, 4, 5, 9, 10, 11, 12, 16, 19, 21, 22, 23, 24, 26, 66, 74 and 76 obtained according to Formulation Example 1 was diluted with water so that the active ingredient concentration came to 50 ppm to prepare a test liquid for each compound.

On the bottom of a polyethylene cup of 5 cm in diameter was placed a filter paper, to which the test liquid had been prepared as described above, was added dropwise in an amount of 1 ml. One germinated seed of corn and 30 to 50 eggs of *Diabrotica undecimpunctata* (southern corn rootworm) was

placed on the filter paper in the polyethylene cup, which was then kept covered and left in a room at 25°C. On the 6th day after, the number of surviving larvae of *Diabrotica undecimpunctata* was examined.

As a result, in the treatment with each of the compounds described above, the number of surviving pests on the 6th day after was 0.

Test Example 5 Pesticidal Test against *Musca domestica*

Each formulation of the compound 1, 3, 4, 10, 11, 15, 17, 22, 24, 30, 31, 32, 33, 34, 35, 36, 37, 39, 40, 41, 42, 43, 45, 46, 47, 52, 55, 56, 57, 58, 59, 60, 64, 65, 66, 67, 68, 69, 71, 74, 75, 79, 82, 84, 89, 90, 92, 101, 102, 105, 107, 108, 109, 110, 111, 114, 115 and 120 obtained according to Formulation Example 5 was diluted with water so that the active ingredient concentration came to 500 ppm to prepare a test liquid for each compound.

On the bottom of a polyethylene cup of 5.5 cm in diameter was placed a filter paper on the same size, to which the test liquid had been prepared as described above, was added dropwise in an amount of 0.7 ml, and 30 mg of sucrose as a bait was placed on it. Ten female adults of *Musca domestica* (house fly) were set free in the polyethylene cup, which was then kept covered. After 24 hours, their survival was examined to determine the mortality.

As a result, in the treatment with each of the compounds described above, it was exhibited the mortality of 100%.

Test Example 6 Pesticidal Test against German cockroach

Each formulation of the compound 1, 2, 3, 4, 5, 9, 10, 11, 12, 15, 16, 17, 23, 30, 31, 32, 33, 36, 39, 40, 41, 42, 43, 46, 47, 52, 55, 56, 57, 58, 59, 60, 64, 68, 69, 74, 79, 84, 89, 102, 109, 110, 114, 119, 120 and 121 obtained in Formulation Example 5 was diluted with water so that the active ingredient concentration came to 500 ppm to prepare a test liquid for each compound.

On the bottom of a polyethylene cup of 5.5 cm in diameter was placed

a filter paper on the same size, to which the test liquid had been prepared as described above, was added dropwise in an amount of 0.7 ml, and 30 mg of sucrose as a bait was placed on it. Two male adults of German cockroach (*Blattalla germanica*) were set free in the polyethylene cup, which was then kept covered. After 6 days, their survival was examined to determine the mortality.

As a result, in the treatment with each of the compounds described above, it was exhibited the mortality of 100%.

Test Example 7 Pesticidal Test against *Cullex pipiens pallens*

Each formulation of the compound 1, 2, 3, 4, 5, 6, 7, 9, 10, 11, 12, 13, 15, 16, 17, 19, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 52, 54, 55, 56, 57, 58, 59, 60, 61, 63, 64, 65, 66, 67, 68, 69, 70, 71, 74, 75, 76, 78, 79, 80, 81, 82, 83, 84, 89, 91, 92, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 115, 116, 118 and 121 obtained according to Formulation Example 5 was diluted with water so that the active ingredient concentration came to 500 ppm to prepare a test liquid for each compound.

In 100 ml of ion-exchanged water, the test liquid had been prepared as described above, was added dropwise in an amount of 0.7 ml (the concentration of active ingredient was 3.5 ppm). Twenty final-instar larvae of *Cullex pipiens pallens* (common mosquito) were set free in the solution. After 1 days, their survival was examined to determine the mortality.

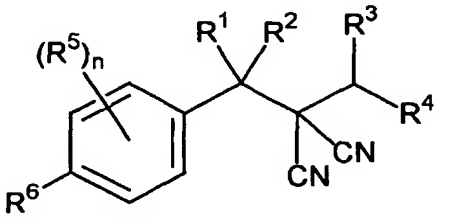
As a result, in the treatment with each of the compounds described above, it was exhibited the mortality of 100%.

Industrial Applicability

The present invention makes it possible to effectively control pests such as insect pests, acarine pests, and nematode pests.

CLAIMS

1. A pesticide composition comprising a malononitrile compound of formula (X):



(X)

wherein R^1 and R^2 are the same or different and independently C_1-C_5 (halo)alkyl, C_1-C_5 (halo)alkyloxy, C_2-C_5 (halo)alkenyl, C_2-C_5 (halo)alkynyl, hydrogen, or cyano;

R^3 and R^4 are the same or different and independently C_1-C_{10} alkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, or hydrogen, or R^3 and R^4 are taken together to form C_2-C_6 (halo)alkylene or C_4-C_6 (halo)alkenylene;

R^5 is halogen, cyano, nitro, C_1-C_4 (halo)alkyl, C_2-C_4 (halo)alkenyl, C_2-C_4 (halo)alkynyl, C_1-C_4 (halo)alkyloxy, C_1-C_4 (halo)alkylthio, C_1-C_4 (halo)alkylsulfinyl, C_1-C_4 (halo)alkylsulfonyl, C_1-C_4 (halo)alkylcarbonyl, C_1-C_4 (halo)alkyloxycarbonyl, C_1-C_4 (halo)alkylcarbonyloxy, phenyloxy, or phenylthio, in which the phenyloxy and phenylthio groups may optionally be substituted with halogen or C_1-C_3 alkyl;

n is an integer of 0 to 4;

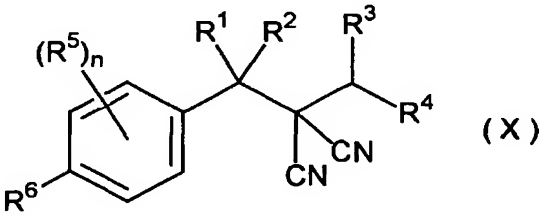
R^6 is hydrogen, halogen, cyano, nitro, C_1-C_4 (halo)alkyl, C_2-C_4 (halo)alkenyl, C_2-C_4 (halo)alkynyl, C_1-C_4 (halo)alkyloxy, C_1-C_4 (halo)alkylthio, C_1-C_4 (halo)alkylsulfinyl, C_1-C_4 (halo)alkylsulfonyl, C_1-C_4 (halo)alkylcarbonyl, C_1-C_4 (halo)alkyloxycarbonyl, C_1-C_4 (halo)alkylcarbonyloxy, phenyloxy, or phenylthio, in which the phenyloxy and phenylthio groups may optionally be substituted with halogen or C_1-C_3 alkyl;

or R^5 and R^6 are taken together to form methylenedioxy;

with the provisos that when R^6 is hydrogen, then n is an integer of 1 to 4 and that when n is 2 or more, then R^5's are the same or different from each other; as an active ingredient, and a carrier.

2. The pesticide composition according to claim 1, wherein a containing amount of the malononitrile compound is 0.1% to 95% by weight.

3. A pest controlling method comprising applying an pesticidally effective amount of a malononitrile compound of formula (X):



(X)

wherein R^1 and R^2 are the same or different and independently C_1-C_5 (halo)alkyl, C_1-C_5 (halo)alkyloxy, C_2-C_5 (halo)alkenyl, C_2-C_5 (halo)alkynyl, hydrogen, or cyano;

R^3 and R^4 are the same or different and independently C_1-C_{10} alkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, or hydrogen, or R^3 and R^4 are taken together to form C_2-C_6 (halo)alkylene or C_4-C_6 (halo)alkenylene;

R^5 is halogen, cyano, nitro, C_1-C_4 (halo)alkyl, C_2-C_4 (halo)alkenyl, C_2-C_4 (halo)alkynyl, C_1-C_4 (halo)alkyloxy, C_1-C_4 (halo)alkylthio, C_1-C_4 (halo)alkylsulfinyl, C_1-C_4 (halo)alkylsulfonyl, C_1-C_4 (halo)alkylcarbonyl, C_1-C_4 (halo)alkyloxycarbonyl, C_1-C_4 (halo)alkylcarbonyloxy, phenyloxy, or phenylthio, in which the phenyloxy and phenylthio groups may optionally be substituted with halogen or C_1-C_3 alkyl;

n is an integer of 0 to 4;

R^6 is hydrogen, halogen, cyano, nitro, C_1-C_4 (halo)alkyl, C_2-C_4 (halo)alkenyl, C_2-C_4 (halo)alkynyl, C_1-C_4 (halo)alkyloxy, C_1-C_4 (halo)alkylthio, C_1-C_4 (halo)alkylsulfinyl, C_1-C_4 (halo)alkylsulfonyl, C_1-C_4 (halo)alkylcarbonyl, C_1-C_4 (halo)alkyloxycarbonyl, C_1-C_4 (halo)alkylcarbonyloxy, phenyloxy, or phenyl-

thio, in which the phenyloxy and phenylthio groups may optionally be substituted with halogen or C_1-C_3 alkyl;

or R^5 and R^6 are taken together to form methylenedioxy;

with the provisos that when R^6 is hydrogen, then n is an integer of 1 to 4 and that when n is 2 or more, then R^6's are the same or different from each other; to pests or habitats of pests.

4. The pest controlling method according to claim 3, wherein R^6 is halogen, cyano, nitro, C_1-C_4 haloalkyl, C_1-C_4 haloalkyloxy or C_1-C_4 haloalkylthio.

5. The pest controlling method according to claim 3, wherein R^3 and R^4 are the same or different and independently C_1-C_5 alkyl, C_2-C_5 alkenyl, C_2-C_5 alkynyl, or hydrogen, or R^3 and R^4 are taken together to form C_2-C_6 (halo)alkylene.

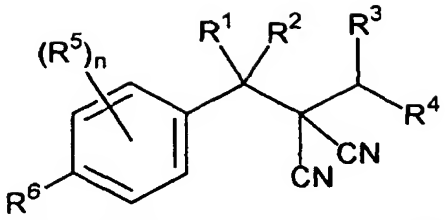
6. The pest controlling method according to claim 3, wherein R^1 and R^2 are both hydrogen.

7. The pest controlling method according to claim 3, wherein R^1 and R^2 are the same or different and independently C_1-C_3 (halo)alkyl, C_1-C_3 (halo)alkyloxy, C_2-C_4 (halo)alkenyl, C_2-C_4 (halo)alkynyl, hydrogen, or cyano; R^5 and R^6 are the same or different and independently halogen, cyano, nitro, C_1-C_3 haloalkyl, C_1-C_3 haloalkyloxy, C_1-C_3 (halo)alkylthio, C_1-C_3 (halo)alkylsulfinyl, C_1-C_3 (halo)alkylsulfonyl, C_1-C_3 (halo)alkylcarbonyl, or C_1-C_3 haloalkyloxycarbonyl.

8. The pest controlling method according to claim 7, wherein R^3 is hydrogen and R^4 are vinyl, allyl, ethyl, 3-butenyl and 1-propenyl.

9. The pest controlling method according to claim 3, wherein the pests are insect pests.

10. Use of a malononitrile compound of formula (X):



(X)

wherein R^1 and R^2 are the same or different and independently C_1-C_5 (halo)-alkyl, C_1-C_5 (halo)alkyloxy, C_2-C_5 (halo)alkenyl, C_2-C_5 (halo)alkynyl, hydrogen, or cyano;

R^3 and R^4 are the same or different and independently C_1-C_{10} alkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, or hydrogen, or R^3 and R^4 are taken together to form C_2-C_6 (halo)alkylene or C_4-C_6 (halo)alkenylene;

R^5 is halogen, cyano, nitro, C_1-C_4 (halo)alkyl, C_2-C_4 (halo)alkenyl, C_2-C_4 (halo)alkynyl, C_1-C_4 (halo)alkyloxy, C_1-C_4 (halo)alkylthio, C_1-C_4 (halo)-alkylsulfinyl, C_1-C_4 (halo)alkylsulfonyl, C_1-C_4 (halo)alkylcarbonyl, C_1-C_4 (halo)alkyloxycarbonyl, C_1-C_4 (halo)alkylcarbonyloxy, phenyloxy, or phenylthio, in which the phenyloxy and phenylthio groups may optionally be substituted with halogen or C_1-C_3 alkyl;

n is an integer of 0 to 4;

R^6 is hydrogen, halogen, cyano, nitro, C_1-C_4 (halo)alkyl, C_2-C_4 (halo)-alkenyl, C_2-C_4 (halo)alkynyl, C_1-C_4 (halo)alkyloxy, C_1-C_4 (halo)alkylthio, C_1-C_4 (halo)alkylsulfinyl, C_1-C_4 (halo)alkylsulfonyl, C_1-C_4 (halo)alkylcarbonyl, C_1-C_4 (halo)alkyloxycarbonyl, C_1-C_4 (halo)alkylcarbonyloxy, phenyloxy, or phenylthio, in which the phenyloxy and phenylthio groups may optionally be substituted with halogen or C_1-C_3 alkyl;

or R^5 and R^6 are taken together to form methylenedioxy;

with the provisos that when R^6 is hydrogen, then n is an integer of 1 to 4 and that when n is 2 or more, then R^5's are the same or different from each other; as an active ingredient of a pesticide composition.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP 02/04450

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A01N37/34 A01N37/36 A01N37/38 A01N37/42 A01N41/10
A01N43/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 178 473 A (CIBA LIMITED) 21 January 1970 (1970-01-21) page 1, line 9 - line 42 page 1, line 55 -page 2, line 5; table example 6	1-10
A	US 3 527·785 A (NISHIZAWA YOSHIHIKO ET AL) 8 September 1970 (1970-09-08) column 1, line 25 - line 62 column 2, line 20 - line 63; example 3 test examples 2 and 3	1-10
A	US 3 694 483 A (CAHOY ROGER P ET AL) 26 September 1972 (1972-09-26) column 1, line 5 - line 24; table	1-10

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 September 2002	08/10/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Muellners, W

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP 02/04450

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 250 798 A (SHULGIN ALEXANDER T) 10 May 1966 (1966-05-10) column 1, line 10 - line 34 column 3, line 5 -column 4, line 4	1-10
A	US 3 551 573 A (HOWE ROBERT K ET AL) 29 December 1970 (1970-12-29) column 1, line 45 -column 2, line 54 column 8, line 25 - line 27; table column 9, line 42 - line 50; table 1	1-10

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/JP 02/04450

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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